

ENCYCLOPEDIA
OF
RENEWABLE
ENERGY

JAMES G. SPEIGHT

Encyclopedia of Renewable Energy

Scrivener Publishing

100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Publishers at Scrivener

Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

Encyclopedia of Renewable Energy

James G. Speight



WILEY

This edition first published 2022 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
© 2022 Scrivener Publishing LLC
For more information about Scrivener publications please visit www.scrivenerpublishing.com.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <http://www.wiley.com/go/permissions>.

Wiley Global Headquarters

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-36367-5

Cover Images: Green Abstract Background | Nnorozoff | Dreamstime.com

Cover design by Kris Hackerott

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Contents

Introduction	xxxvii
A	1
Absorption	1
Absorption Cleaning	2
Absorption Dehydration	3
Absorption Oil	4
Absorption Process	4
Absorption Tower	5
Accuracy and Precision in Analysis	5
Acetogenesis	7
Acid Catalyst	8
Acid Deposition	8
Acid Gas	9
Acid Gas Removal	10
Acid Gas Removal Processes	12
Acid Gas Scrubbing – Basic Solid or Solution	14
Acid Gas Scrubbing – Wet Scrubbers	15
Acid Hydrolysis	16
Acidity and Alkalinity	17
Acid Number	18
Acidogenesis	18
Acidogenic Digestate	19
Acid Rain	21
Acid Rain – Formation	22
Acid Rain – Mitigation	23
Acid Treating	23
Acid Value	24
Activated Sludge Process	25
Additives – Catalysts in Combustion Systems	25
Additives – Fuels	27
Add-On Environmental Control Methods	27
Adip Process	28
Adsorption	29
Adsorption Isotherm	29
Adsorption Process	31
Advanced Cycloning	32
Advanced Flue Gas Desulfurization	32
Aerobic Digestion	32
Aerosols	34
Agave Bagasse	34

Agricultural Residue	35
Agricultural Residue – Types	37
Agricultural Waste	38
Agrofuel	38
Air Emissions	39
Air Emissions – Biomass Plant	40
Air Flotation Processes	40
Air Pollution	41
Alcohol Blended Fuel	41
Alcohol-Diesel Emulsion	42
Alcohol Fuels	42
Alcohol Fuels – Ethanol	43
Alcohol Fuels - Methanol	45
Alcohol Fuels – Propanol and Butanol	46
Alcohols	47
Alcohols – Combustion	48
Alcohols – Corrosivity	49
Alcohols – From Waste	50
Alcohols – Production	50
Algaculture	53
Algae	53
Algae Fuels	54
Algae Fuels – Extraction	55
Algal Blooms	55
Alkali Washing Process	56
Alicyclic Hydrocarbons	56
Aliphatic Hydrocarbons	57
Alkalinity	59
Alkaloids	59
Alkanes	60
Alkanolamines	62
Alkazid Process	62
Alkenes	63
Alpha Decay	64
Alpha Particle	64
Alternate Fuels	65
Alternate Fuels – Gaseous Fuels	65
Alternate Fuels – Liquid Fuels	66
Alternate Fuels - Production	67
Alternate Fuels – Solid Fuels	68
Alternative Energy	68
Amine Washing	68
Ammonia	70
Anaerobic Digestion	70
Anaerobic Digestion – Gas Production	72
Animal Waste	73
Annual Removal	73
Apparent Density	74
Aquaculture	74
Aquasphere	75
Aquatic Organisms	81

Aquatic Plants	82
Aquiclude, Aquitard, Aquifuge	82
Aquifer	83
Aromatic Hydrocarbons	84
Arsenic and Selenium	84
Asabe Standard X593	85
Ash	85
Ash Analysis	86
Ash Composition	86
Ash Content	87
Ash Content – Biomass	89
As-Received Moisture	90
Atmosphere	90
Atmospheric Equivalent Boiling Point	94
Atomic Energy	94
Attapulgius Clay	95
Attrition Catalyst	95
Azeotrope	95
Azeotropic Distillation	96

B	99
Bacteria	99
Bacterial Mining	99
Bagasse	100
Bagasse Briquettes	101
Baghouse	101
Baghouse Filter	102
Barrel	102
Barrel of Oil Equivalent	103
Basic Nitrogen	103
Basic Sediment and Water	104
Batch-Type Processes	105
Baumé Gravity	105
Bauxite	106
Bauxite Treating Process	107
Beavon Process	107
Benchmark Crude Oil	107
Beta Decay	108
Beta Particle	109
Bioalcohol	109
Biocatalysts	111
Biochar	111
Biochemical Conversion	112
Biochemical Oxygen Demand	113
Biochemicals	113
Biochemicals - Production	114
Bioconversion	120
Bioconversion Platform	121
Biodegradation	122
Biodegradation – In Situ	124
Biodegradation Processes	125

Biodegradation – Slurry Phase	127
Biodegradation – Solid Phase	127
BioDeNOx Process	128
Biodesulfurization	128
Biodiesel	129
Biodiesel Feedstocks	131
Biodiesel – Production and Properties	133
Biodiesel – Technical Standards	135
Biodiesel – Transesterification	137
Biodiesel – Transesterification, Catalytic	138
Biodiesel – Transesterification, Supercritical Methanol	139
Biodiesel – Transesterification, Reaction Parameters	139
Bioenergy	140
Bioenergy Crops	140
Bioenergy System	141
Bioethanol	141
Bioethanol Production	142
Bioethers	142
Biofiltration	143
Biofuels	144
Biofuels - Classification	146
Biofuels - Feedstocks	148
Biofuels – First Generation	149
Biofuels – From Synthesis Gas	149
Biofuels – Liquid	150
Biofuels – Platforms	151
Biofuels – Production	152
Biofuels – Properties, Variations with Source	152
Biofuels – Second Generation	155
Biofuels – Specifications and Performance	156
Biofuels – Third Generation	157
Biofuels – Use	158
Biogas	158
Biogas – Upgrading	160
Biogenic Coal Bed Methane	162
Biogeochemical Cycles	162
Biohydrogen	163
Biohydrogen – Production	164
Biological Action	164
Biological Alcohol	165
Biological Conversion	165
Biological Conversion – Aerobic Digestion	165
Biological Conversion – Anaerobic Digestion	166
Biological Hydrogen Production	169
Biomass	169
Biomass Ash	172
Biomass Chemistry	172
Biomass Combustion	174
Biomass Composition and Properties	174
Biomass – Conversion Technologies	176
Biomass-Derived Carbon	177

Biomass – Direct Combustion	178
Biomass – Drying	178
Biomass Energy	180
Biomass Energy Systems	181
Biomass – Extraction	182
Biomass Feedstocks	182
Biomass – Fermentation	183
Biomass Fuel	183
Biomass Fuel – Characteristics	184
Biomass – Gasification	184
Biomass – Gasification Principles	186
Biomass – Gasification Process	186
Biomass – Gasification Reactors	187
Biomass – Herbaceous	189
Biomass – Land Requirements	190
Biomass – Liquefaction	191
Biomass Power	191
Biomass – Power Facility	191
Biomass Properties	192
Biomass – Pyrolysis	192
Biomass – Synthesis Gas Production	193
Biomass to Energy	195
Biomass to Liquids	196
Biomass Waste	198
Bio-oil	200
Bio-oil – Upgrading	202
Bio-oxidation	202
Biophotolysis	203
Biopower	203
Bioprocess	204
Bioreactor	205
Biorefinery	206
Bio-SCOT Process	209
Bioscrubbing	209
Bitumen	209
Black Liquor	210
Blended Fuels	211
Blending	211
Blue Gas	212
Blue Water Gas	212
Boiler Slag	212
Boiling Water Reactor	213
Bone Dry	213
Boson	213
Bottom Ash	213
Bottoming Cycle	214
Bottom Sediment and Water	214
Boudouard Reaction	214
Breeder Reactor	215
BRI Process	215
Briquette	215

Briquette Binder	216
Briquette Manufacture	217
Briquette Properties	217
Briquetting Processes	218
Bromine Number	219
BTEX	219
BTU	220
BTX	220
Bubble Point	220
Bubbling Fluidized Bed Gasifier	221
Bulk Density	221
Bunker	222
Bunker Fuel Oil	222
Butane	222
Butane Dehydrogenation	223
Butane Vapor-Phase Isomerization	224
Butanol	224
Butene	225
Butene Dehydrogenation	225

C	227
C ₁ , C ₂ , C ₃ , C ₄ , C ₅ Fractions	227
Calorific Value	227
Camelina	227
Canola Oil	228
Capillary Forces	228
Capillary Number	229
Capillary Pressure	229
Carbohydrates	229
Carbonate Washing and Water Washing	230
Carbonate Washing Process	230
Carbon Cycle	231
Carbon Dioxide	231
Carbon Dioxide Balance	231
Carbon Dioxide Gasification	232
Carbon Dioxide Recovery	232
Carbonization	233
Carbon Monoxide	234
Carbon Residue	234
Carbon Sink	234
Carbo-V Process	235
Carbureted Blue Gas	236
Carbureted Water Gas	236
Catalysts	236
Catalysts – Activity	237
Catalyst – Deactivation	238
Catalyst Fouling	238
Catalysts – Hydrogen Production	239
Catalysts – Methanation	240
Catalyst Poisoning	241
Catalyst Regeneration	241

Catalysts – Selectivity and Conversion	242
Catalyst Sintering	242
Catalysts – Solid Acid	242
Catalyst Stripping	243
Catalytic Cracking	243
Catalytic Cracking Chemistry	245
Catalytic Cracking Processes	246
Catalytic Cracking – Process Parameters	247
Catalytic Gas Conversion Process	249
Catalytic Gasification	249
Catalytic Oxidation Processes	250
Catalytic Reforming	251
Catalytic Reforming - Catalysts	252
Catalytic Reforming – Processes	253
Catalytic Three-Phase Reactors	254
Catalytic Transesterification	254
Caustic Scrubbing	255
Caustic Treating	255
Cellulose	256
Cellulosic Biomass	258
Cellulosic Ethanol	259
Cellulosic Materials	260
Centrifugal Separation	260
Cetane Index	261
Cetane Number	261
Char	262
Charcoal and Charcoal Briquettes	262
Chemical Composition of Biomass	264
Chemical Precipitation	265
Chemical Reaction Rates	266
Chemicals Reactive with Water	266
Chemical Treating	267
Chemical Waste	268
Chemicals from Biomass	268
Chemisorption	270
Chemistry in the Aquasphere	271
Chemistry in the Atmosphere	272
Chemistry in the Geosphere	274
Chemsweet Process	275
Chinese Tallow Tree	276
Circulating Fluidized Bed Gasifier	276
Claus Process	276
Clay Minerals	278
Clay Treating Process	279
Climate Change	279
Closed-Loop Biomass	281
Coagulation	281
Coarse Materials	282
Co-Combustion	282
COED/COGAS Process	282
Co-Firing	283

Cogeneration	283
Cohesive Energy Density	284
Cold Pelletizing	284
Combustion	284
Combustion - Chemistry	285
Combustion – Direct	287
Combustion – Effect of Additives and Catalysts	288
Combustion – Environmental Aspects	289
Combustion – Fluidized Bed	292
Combustion – Fouling	292
Combustion – Heat Balance	293
Combustion – Ignition	294
Combustion – Influence of Feedstock Quality	294
Combustion – Mechanism	294
Combustion – Soot Formation	295
Combustion – Surface Effects	296
Combustion Technologies	296
Combustion – Types of Combustors	298
Combustion Zone	300
Combustion Plants	300
Complete Mix Digester	302
Concentrated Acid Hydrolysis	302
Condensation	303
Coniferyl Alcohol	303
Conservation	304
Conservation Reserve Program	304
Contaminant	304
Contingent Resources	304
Conventional Fuel Sources	305
Conversion Pathways	306
Conversion Processes – Biochemical	306
Conversion Processes – Biomass Properties	307
Conversion Processes – Combustion	308
Conversion Processes – Gasification	309
Conversion Processes - Pyrolysis	310
Conversion Processes – Thermal	311
Copper Sweetening Process	312
Cord	312
Cordgrass	313
Coriolis Force	313
Corn	314
Corn Ethanol	314
Corn Oil	315
Corn Stalks and Wheat Straw	315
Corn-to-Ethanol Process	315
Corrosion	316
Corrosion by Fuel Ash	316
p-Coumaryl Alcohol	317
Counter-Current Fixed Bed Gasifier	317
Covered Lagoon Digester	317
Cracking	318

Cropland	319
Crops	319
Crops – Residues	321
Cross Draft Gasifier	321
Crude Oil	322
Cryogenic Dehydration	322
Cryogenic Equipment	322
Cryogenic Expander Process	323
Cryogenic Separation	323
Cryosphere	323
Crystallization	324
CTSL Process	324
Cull Tree	325
Cultivated Summer Fallow	325
Current Reserves	325
Cyclone Separation	326
Cycloparaffin Hydrocarbons	326

D	329
Darcy's Law	329
DEA	329
Dehydration	330
Dehydration – Glycol Process	330
Dehydration – Solid Desiccant	331
Dehydrator Systems	332
Delignification	333
Densification	333
Deposition	334
Descending Bed Reactor	335
Desiccant Dehydrators	335
Desorption	335
Deuterium	336
Devolatilization	337
Dewatering	337
Diesel-Alcohol Emulsion	340
Diesel Cycle	340
Diesel Engine	341
Diesel Fuel	341
Diesel Index	342
Digester	342
Digestion	344
Dimethyl Ether	344
Direct Biofuels	345
Direct Combustion	345
Direct-Fired Biomass	346
Dispersion	347
Dissolution	348
Distillation	349
Distribution in the Environment	351
Domestic Waste	355
Downdraft Combustion	356

Downdraft Gasifier	357
Downflow Fixed Bed Reactor	357
Drizo Process	358
Drop Tube Furnace	359
Dry-Ash-Free Basis	359
Dry Deposition	359
Drying	360
Dry Point	361
Dry Sorption Processes	362
Dust Collectors	362
Dust Control	363
Dustiness Index	363
Dutch Oven Furnace	364
E	365
E85	365
Earth System	365
Ebullated Bed Reactor	366
Ecological Cycles	366
Ecosystem	368
E-Gas Process	369
Electrical Energy	369
Electricity Generation – Equipment	369
Electricity Generation from Conventional Fuels	370
Electricity Generation from Crops	370
Electricity Generation from Waste	371
Electricity Generation from Wood	371
Electricity Generator	371
Electrochemical Processes	372
Electrolysis	372
Electron	373
Electronic Waste	373
Electrostatic Precipitator	374
Emissions and Effluents	375
Emission Control	380
Emulsification	381
Emulsifying Agents	382
Endothermic Reaction	383
Energy	383
Energy Balance	384
Energy Conservation	384
Energy Content	385
Energy Crops	385
Energy Crops – Grasses	388
Energy Crops – Oilseed Crops	389
Energy Crops – Residual Herbaceous Biomass	389
Energy Crops – Short Rotation Woody Crops	390
Energy Crops – Sugar Crops	390
Energy Density	391
Energy-Efficiency Ratio	391
Energy Production from Crops	392

Energy Production from Wood	397
Energy Sources	398
Enersludge Process	400
Enrichment	400
Entrained-Bed Combustion	401
Entrained-Bed Gasifier	401
Entrained-Flow Process	402
Entrained Flow Reactor	402
Environment	402
Environmental Ethics	403
Environmental Issues	403
Environmental Issues – Biomass Use	405
Enzymatic Hydrolysis	406
Enzymes	407
Esterification	408
Ethanol	409
Ethanol Production	411
Ethanol Production – Feedstocks	412
Ethanol Production – From Corn	413
Ethanol Production – From Lignocellulosic Feedstocks	414
Ethanol Production – From Wood	415
Ethanol Production - Yields	415
Ethyl Alcohol	416
Evaporation	416
Evaporation Processes	418
Exosphere	418
Exothermic Reaction	419
Explosive Limits	419
Extraction	420
Extractive Distillation	420
Explosive Limits	421
Extra Heavy Crude Oil	421
Extraneous Mineral Matter	422
ExxonMobil AGC-21 Process	422
F	423
Fabric Filter	423
Fast-Neutron Reactor	423
Fast Pyrolysis	424
Fat Oil	424
Fats And Greases	424
Fatty Acids	424
Feedstock	427
Fermentation	427
Fermentation Chemistry	429
Fermentation Plants	430
Ferrel Cell	430
Ferrox Process	431
Fibers	431
Filters	432
Filter Tubes	433

Filtration	433
Fire Point and Flash Point	434
Firewood	434
Fischer-Tropsch Process	435
Fischer-Tropsch Process – Catalysts	436
Fischer-Tropsch Chemicals	436
Fischer-Tropsch Process	437
Fischer-Tropsch Process – Chemistry	439
Fischer-Tropsch Process – Commercial Processes	440
Fischer-Tropsch Process – Products	442
Fischer-Tropsch Process – Product Separation and Upgrading	443
Fischer-Tropsch Process – Reactors	444
Fixed-Bed Incinerator or Moving-Grate Incinerator	444
Fish Oil	445
Fixed-Bed Process	445
Fixed-Bed Reactor or Moving-Bed Reactor	446
Fixed Carbon	446
Flammability	446
Flammability Range	448
Flash Point	448
Flash Pyrolysis	449
Flash Vaporization	450
Flax and Flaxseed Oil	450
Flexible-Fuel Vehicle	451
Flexsorb Process	451
Flocculation	452
Flue Gas	452
Flue Gas Cleaning	454
Flue Gas Desulfurization	454
Fluid Bed	455
Fluid-Bed Boiler	456
Fluid-Bed Catalytic Cracking	456
Fluid-Bed Catalytic Cracking Unit	457
Fluid-Bed Combustion	457
Fluid-Bed Gasifier	459
Fluid-Bed Incinerator	459
Fluid-Bed Processes	460
Fluid-Bed Reactor	460
Fluid-Bed Thermal Cracking	461
Fly Ash	461
Forage Crop	462
Forest Health	462
Forest Land	462
Forest Residues	463
Fossil Fuel Resources	463
Fouling	464
Fouling Tendency	464
Fractional Composition	466
Fractionation	466
Fractionation – Absorption Methods	467
Fractionation – Adsorption Methods	468

Fractionation – Chemical Methods	468
Fractionation – Distillation Methods	468
Fractionation – Solvent Methods	469
Fuel Cell	470
Fuel Oil	470
Fuels	471
Fuels from Biomass	471
Fuels from Crops	472
Fuels from Waste	473
Fuels from Wood	474
Fuel Wood	475
Fuel Wood – Selection and Preparation	476
Fuel Wood – Use	476
Functional Group	477
Fungi	479
Fusion Energy	480
G	481
Gamma Decay	481
Gas Analysis	481
Gas Cleaning	483
Gas Cleaning – Alkali Washing Processes	485
Gas Cleaning – Biological Methods	485
Gas Cleaning – Chemisorption	486
Gas Cleaning – Effects of Gas Composition	489
Gas Cleaning – Membrane Processes	490
Gas Cleaning – Metal Oxide Processes	491
Gas Cleaning – Methanol Based Processes	491
Gas Cleaning – Molecular Sieve Processes	492
Gas Cleaning – Physical Solvent Processes	493
Gas Cleaning – Process Selection	494
Gas Cleaning – Process Types	495
Gas Cleaning – Removal of Acid Gases	496
Gas Cleaning – Removal of Alkali Metal Salts	504
Gas Cleaning – Removal of Ammonia	504
Gas Cleaning – Removal of Condensable Hydrocarbons	504
Gas Cleaning – Removal of Nitrogen	508
Gas Cleaning – Removal of Particulate Matter	509
Gas Cleaning – Removal of Siloxane Derivatives	509
Gas Cleaning – Removal of Tar	510
Gas Cleaning – Sulfur Recovery Processes	511
Gas Cleaning – Water Removal	512
Gas Compression	515
Gas Condensate	516
Gas-Cooled Reactor	516
Gaseous Effluents	517
Gaseous Fuels	520
Gaseous Fuels from Waste	523
Gaseous Fuels from Waste – Reactors	524
Gaseous Fuels from Wood	524
Gaseous Fuels – High Btu Gas	526

Gas Fuels – Low Btu Gas	526
Gaseous Fuels – Medium Btu Gas	527
Gases and Naphtha	527
Gaseous Hydrocarbons – General Properties	528
Gaseous Pollutants	529
Gaseous Pollutants – Control	529
Gasification	531
Gasification Chemistry	532
Gasification of Biomass	532
Gasification of Biomass – Feedstock Preparation	534
Gasification Reactors	535
Gasifiers	537
Gasifiers – Bubbling Fluidized Bed Gasifier	537
Gasifiers – Circulating Fluidized Bed Gasifier	538
Gasifiers – Cross Draft Gasifier	538
Gasifiers – Downdraft Gasifier	538
Gasifiers – Entrained Bed Gasifier	539
Gasifiers – Fluidized Bed Gasifier	539
Gasifiers – Moving Bed Gasifier	539
Gasifiers – Updraft Gasifier	540
Gas Laws	540
Gas Liquids	544
Gas Liquids – Fractionation	544
Gasohol	545
Gas Oil	545
Gasoline	546
Gas Processing	547
Gas Processing – Chemical Activators	548
Gas Processing – Process Selection	548
Gas Purification	549
Gas Streams	549
Gas-to-Commodity	553
Gas-to-Liquids	553
Gas-to-Power	554
Gas-to-Solid	555
Gas Treating	556
Geochemical Cycles	557
Geohydrology	558
Geological Age	558
Geosphere	559
Geothermal Energy	562
Geothermal Energy – Electricity Generation	564
Geothermal Energy – Environmental Effects	565
Geothermal Gradient	565
Geothermal Heat Pumps	566
Geothermal Power Plants	567
Geothermal Sources	568
Giant Reed Grass	569
Girbotol Process	570
Girdler Process	570
Global Climate Change	572

Glycol-Amine Gas Treating	572
Glycol-Based Processes	573
Glycol Degradation	574
Glycol Dehydration	575
Gober Gas	576
Grain Crops	576
Grasses	576
Grassland Pasture and Range	577
Grease Car	577
Grease Trap	577
Greenhouse Effect	577
Greenhouse Gases	578
Greenhouse Gas Production	578
Gross Sample	579
Groundwater	580
Groundwater Aquifer	581
Growing Stock	582
Guard Bed	582
Guard Bed Reactor	583
Gum	583
Gum Formation	583

H 585

Hadley Cell	585
Halite	585
Hardwood	586
Hazardous Air Pollutant	587
Hazardous Chemicals	588
Hazardous Waste	588
H-Coal Process	589
Heat Balance	589
Heat Capacity	590
Heat Content	590
Heat Exchangers	592
Heating Value	593
Heat of Combustion	593
Heavy Metals	594
Heavy Oil	596
Heavy Water Reactor	596
Helium-3	596
Hemicellulose	597
Hemp	597
Herbaceous Biomass	598
Herbaceous Crops	598
Heteroatom Compounds	599
Heterogeneous Catalyst	599
Heterosphere	600
High-Btu Gas	600
Higher Heating Value	601
High-Temperature Water Splitting	601
Homosphere	602

Horizontal and Vertical Axis Turbines	602
Hot Filtration Test	603
Hot Gas Cleaning	603
Hot Potassium Carbonate Process	603
Humidity	604
Hybrid Poplars	604
Hydrane Process	604
Hydrocarbon and Carbon Monoxide Controls	605
Hydrocarbon Fuels	605
Hydrocarbon Gases – Physical Constants	605
Hydrocarbons	606
Hydrocracking	608
Hydrocracking Catalysts	610
Hydrocracking Chemistry	611
Hydrocracking Processes	612
Hydrodenitrogenation	613
Hydrodesulfurization	613
Hydrodesulfurization Catalysts	614
Hydroelectric Dams	615
Hydroelectric Energy	616
Hydroelectric Power	618
Hydroelectric Power Generation	618
Hydroelectric Power – Turbines	620
Hydrogasification	620
Hydrogen	621
Hydrogen Economy	622
Hydrogen – Environmental Impact	623
Hydrogen Fuel	623
Hydrogen – Production	624
Hydrogen – Production By Pyrolysis	625
Hydrogen Production Chemistry	626
Hydrogen Production Processes	627
Hydrogen Properties	628
Hydrogen Purification	629
Hydrogenation and Hydrolysis Processes	630
Hydrogen Energy	630
Hydrogen Sulfide	632
Hydrogen Sulfide – Control	632
Hydrogen Sulfide Conversion	634
Hydrogen Sulfide Removal	634
Hydrogeology	635
Hydrokinetic Energy	635
Hydrokinetic Power Generation	637
Hydrologic Cycle	637
Hydrolysis and Fermentation of Sugar	638
Hydrolysis – Anaerobic Digestion	638
Hydrolysis – Lignocellulosic Materials	638
Hydropower	639
Hydroprocessing	640
Hydroshear Emulsification	640
Hydrothermal Upgrading	640

Hydrotreating	641
Hydrotreating Catalysts	642
Hydrotreating Processes	644
Hydrotreating – Process Parameters	645
Hydrous Pyrolysis	648
Hydroxylation	648
Hygas Gasifier	649
Hypro Process	649
I	651
Ideal Gas	651
Ideal Gas Law	651
IFPEXOL Process	652
IFP Spent Tire Depolymerization Process	652
Ignifluid Combustion System	653
Ignitability	653
Ignitable Liquid	653
Immiscibility	654
Immiscibility – Test Methods	654
Impulse Turbines	654
Incinerator	655
Inclined Grate Furnace	656
Incompatibility	657
Indirect Liquefaction	658
Indirect Liquefaction Processes	658
Indirectly Heated Gasifiers	659
Industrial Chemicals	660
Industrial Waste	662
Inertial Separator	662
Inferred Reserves	663
Inherent Mineral Matter	663
Inorganic Chemicals	663
Inorganic Chemical Transformation Reactions	664
Inorganic Chemical Transformation Reactions – Hydrolysis Reactions	666
Inorganic Chemical Transformation Reactions – Photolysis Reactions	666
Inorganic Chemical Transformation Reactions – Radioactive Decay	668
Inorganic Chemical Transformation Reactions – Rearrangement Reactions	668
Inorganic Chemical Transformation Reactions – Redox Reactions	669
Inorganic Matter	669
Instability and Incompatibility	670
Instability and Incompatibility – Methods For Determining	670
Iodine Number	671
Ionic Liquids	672
Iogen Process	674
Iron Oxide Process	674
Iron Oxide Slurry Process	676
Iron Oxide Suspension Process	677
Iron Sponge Process	677
Isotopes	678
ITSL Process	679

J	681
Jatropha	681
Jatropha Oil	681
Jerusalem Artichoke	682
K	683
Kerosene	683
Kinematic Viscosity	684
Koppers-Totzek Gasifier	685
Koppers-Totzek Gasifier – Biomass Gasification	685
Koppers-Totzek Process	686
Kopp's Law	687
Kraft Process	687
L	689
Landfill Classification	689
Landfill Gas	691
Landfilling	702
Landfill Leachate	702
Landfill Leachate Management	703
Landfill Mining	704
Landfill Sites	705
Landfill Sites – Bioreactor	706
Landfill Sites – Construction and Debris	707
Landfill Sites – Hazardous Waste	707
Landfill Sites – Manual	707
Landfill Sites – Municipal Solid Waste	708
Landfill Sites – Sanitary	708
Landfill Sites – Surface Impoundment	708
Landfill Waste – Gasification	709
Landfill Waste – Power Generation	709
Leaching	710
Lean Gas and Rich Gas	711
Life Cycle Impacts	712
Light Ends	712
Light Hydrocarbons	714
Lightning	714
Lignans	715
Lignin	715
Lignocellulose	718
Limnology	718
Linseed oil	719
Lipids	719
Liquefaction	720
Liquid Absorption Processes	720
Liquid Biofuels	721
Liquid Fuels	721
Liquid Fuels from Biomass	721
Liquid Fuels From Waste	724
Liquid Fuels from Wood	727
Liquid Fuels – Biodiesel	729
Liquid Fuels – Ethanol	729

Liquid Fuels – Methanol	732
Liquid Fuels – Propanol and Butanol	732
Liquid-Liquid Extraction	733
Lithosphere	733
Logging Residue	733
Logs and Woodchips	734
Low-Btu Gas	734
Lower Explosive Limit	735
Lower Flammability Limit	736
Lower Heating Value	736
Low-Heat Content Gas	736
Low-Temperature Char	737
Lurgi Combined Reforming Process	737
Lurgi Dry Ash Gasifier	738
Lurgi Process	739
Lurgi Slagging Gasifier	739
Lye Treating Process	740
M	741
M85	741
Macroalgae	742
Maize	742
Manufactured Gas	743
Material Balance	743
MDEA	744
MEA	744
Mechanical Energy	745
Medium-Btu Gas	745
Medium Heat Content Gas	745
Membrane	746
Membrane Permeation	746
Membrane Processes	747
Mercaptans	748
Mercury	749
Meson	750
Mesosphere	750
Metal Oxide Processes	750
Methanation	751
Methanation Catalysts	751
Methane	752
Methane Number	753
Methanogenesis	753
Methanogens	755
Methanol	756
Methanol – Production	758
Methanol – Properties	759
Methanol – Reactions	761
Methanol-Based Processes	762
Methanol-to-Gasoline Process	763
Methanol-to-Olefins Process	763
Methanol-to-Olefins-to-Gasoline Process	764

Methyl Alcohol	764
Microalgae	765
Microchannel Reactor	765
Mill Residue	765
Minerals	766
Miscanthus	768
Miscibility	769
Mixalco Process	769
Mixing	769
Mobile Bed Scrubber	770
Mobil-M Process	770
Moisture in Biomass	771
Molten Bath Gasifiers	772
Molten Salts	773
Municipal By-Products	773
Municipal Solid Waste	774
Municipal Solid Waste – Energy From	776
Municipal Waste	777
Muon	778
Mustard Seed	778

N	781
Naft	781
Naphtha	781
Naphthalene and Polynuclear Aromatic Hydrocarbons	782
Naphthenes	784
Natural Gas	784
Neem Oil	786
Neutralization Number	786
Neutron	787
Neutron Moderator	787
Nitrogen Cycle	787
Nitrogen Oxides	788
Nitrogen Oxides Control	788
Noise Control	788
Non-Hydrocarbon Components	788
Non-Methane Hydrocarbons	789
Non-Conventional Fuel Sources	790
NOx	790
Nuclear Energy	791
Nuclear Energy – Environmental Impact	793
Nuclear Fission	794
Nuclear Fusion	795
Nuclear Power	797
Nuclear Power Plant	798
Nuclear Reactor	799
Nuclear Reactor – Boiling Water Reactor	801
Nuclear Reactor – Breeder Reactor	801
Nuclear Reactor - Decommissioning	802
Nuclear Reactor – Fast Neutron Reactor	802
Nuclear Reactor – Gas-Cooled Reactor	803

Nuclear Reactor – Heavy Water Reactor	803
Nuclear Reactor – Pressurized Water Reactor	804
Nuclear Safety	804
Nuclear Waste Management	805
O	807
Occidental Flash Pyrolysis Process	807
Ocean Currents	807
Ocean Energy	808
Octane Number	810
Octane Rating	811
Oil-Bearing Plants	812
Oils, Fats, and Waxes	812
Okra	813
Olamine	814
Olamine Processes	814
Olefin Hydrocarbons	816
Open Core Gasifier	819
Open-Loop Biomass	819
Organic Chemicals	819
Organic Chemical Transformation Reactions	820
Organic Chemical Transformation Reactions – Addition and Elimination Reactions	821
Organic Chemical Transformation Reactions – Hydrolysis Reactions	821
Organic Chemical Transformation Reactions – Photolysis Reactions	822
Organic Chemical Transformation Reactions – Rearrangement Reactions	822
Organic Chemical Transformation Reactions – Redox Reactions	823
Organic Chemical Transformation Reactions – Substitution Reactions	824
Organic Matter	827
Organic Solvents	828
Other Energy Resources	828
Oxidation	829
Oxygen	830
Oxygenated Gasoline	831
Oxygenates	831
Oxygen Compounds	831
Oxygen Cycle	832
Oxygen Delignification	832
Ozone Layer	834
P	835
Packed Bed	835
Packed Bed Reactor	835
Packed-Bed Scrubber	836
Paraffin Hydrocarbons	836
Paracoumaryl Alcohol	837
Partial Oxidation	837
Particulate Matter	838
Particulate Matter Control	839
Particulate Matter Removal	839
Peanut Oil	840
Peat	841
Peat Swamp and Peat Swamp Forest	841

Pelletization	842
Pellets and Briquettes	842
Percolation Filtration Process	843
Perennial Systems for Biofuel Production	843
Peri-Condensed Aromatic Compounds	844
Periodic Table of the Elements	844
Permeability	845
Petrochemicals	846
pH	849
Phenol	850
Phosphate Desulfurization	850
Photolytic Oxidation Process	851
Photon	851
Photosynthesis	851
Photovoltaics	852
Photovoltaic Cells	853
Physical Solvent Processes	854
Physical Transformation Reactions	855
Physical Transformation Reactions – Absorption	856
Physical Transformation Reactions – Adsorption	856
Physical Transformation Reactions – Dilution	857
Physisorption	858
Pile Burners	858
Pipeline Corrosion	858
Pipeline – Protective Coating	859
Pipeline Transportation	859
Pitch	861
Plant Fibers	861
Plasma	861
Platform Chemicals	863
Plug Flow Digester	864
Plutonium	864
Polar Cell	865
Pollutant	866
Pollution	871
Pollution Control	871
Polychlorobiphenyls	871
Polycyclic Aromatic Hydrocarbons	872
Polycyclic Compounds	873
Polymer Waste	875
Polynuclear Aromatic Compounds	876
Pongamia Oil	876
Porosity	876
Porphyrins	877
Positron	878
Possible Reserves	879
Post-Combustion Cleaning	879
Potatoes	880
Potential Reserves	880
Pour Point	881
Precipitation	881

Pressure Swing Adsorption	881
Pressurized Water Reactor	882
Primary Biomass Feedstock	883
Primary Gasification	883
Primary Wood-Using Mill	884
Probable Reserves	884
Process Gas	884
Process Selection – Gas Treating	886
Process Selectivity	886
Process Wastes	886
Producer Gas	887
Product Analysis	888
Product Analysis – Chromatographic Methods	893
Product Analysis – Spectroscopic Methods	895
Product Blending	899
Product Improvement	900
Production of Organic Matter in Aqueous Environments	900
Product Treating	901
Propane	902
Propanol	904
Propanol and Butanol	904
Proteins	905
Protium	906
Proton	906
Proven Reserves	906
Proximate Analysis	907
P-Series Fuels	907
Pullman-Kellogg Process	908
Pulping	908
Pulpwood	909
Puraspec Process	910
Purisol Process	910
Purox Process	911
Pyridine Bases	911
Pyrolysis	912
Pyrolysis – Biomass	913
Pyrolysis Processes	915
Pyrolysis Oil	918
Q	921
Quality	921
Quench	921
R	923
Radiation	923
Radiation – Types	923
Radioactive Decay	926
Radioactive Isotopes	927
Radioactive Metals	928
Radioactive Waste	929
Radioactivity	931
Radionuclides	933

Rankine Cycle	934
Rapeseed	934
Rapeseed Methyl Ester	935
Rate of Reaction	935
Reactor Types	936
Reburning	937
Recoverable Reserves	938
Recovery Boiler	939
Recovery Processes	939
Rectisol Process	945
Redox Processes	945
Reed Canary Grass	946
Reed Plants	946
Refinery Gas	947
Refinery Waste	948
Refining	949
Refining – Fischer-Tropsch Products	950
Refuse-Derived Fuel	950
Refuse Gas	951
Regenerative and Non-Regenerative Gas Cleaning Processes	951
Removal of Nitrogen-Containing Gases	952
Removal of Sulfur-Containing Gases	953
Renewability	955
Renewable Energy	956
Renewable Energy – Sources	956
Renewable Natural Gas	958
Research Octane Method	958
Reserves	958
Residual Herbaceous Biomass	959
Residual Woody Biomass	960
Residues	960
Resources and Reserves	960
Reverse Osmosis	964
Reversible Chemical Reactions	964
Rhizosphere	965
Rice Straw	965
Rotary Kiln Incinerator	965
Rotation	966
Round Wood Products	966
RTP Process	966
S	969
Saponification Value	969
Sasol Slurry Phase Reactor	969
Sawdust Briquettes	970
SCOT Process	970
Scrap Tires	971
Screening	971
Scrubbers	972
Scrubbing	972
Scrubbing Reagent	973

Seashore Mallow	974
Secondary Biomass Feedstocks	974
Secondary Gasification	974
Sedimentation	975
Sedimentary Strata	975
Selectox Process	976
Selexol Process	977
Separation Processes – Definition and Characteristics	977
Separation Processes – Separation of Solids	978
Settling and Flotation	979
Shell Gasification Process	979
Shell Gasifier	979
Shell-Paques Process	980
Shell-Paques/Thiopaq Process	980
Shell SGP Process	980
Shell SMDS Process	980
Shift Conversion	981
Shift Conversion Catalysts	982
Short Rotation Coppice	982
Short Rotational Coppicing	983
Short Rotation Forestry	983
Sinapyl Alcohol	984
Sizing	984
Slagging, Fouling, and Clinkering	984
Slagging Lurgi Gasifier	985
Sludge	985
Slurry Phase Reactor	985
Smog	986
Smog Formation	987
Sodasol Process	987
Sofnolime RG Process	988
Softwood	988
Softwood Residues	989
Soil	989
Solar Collectors	992
Solar Energy	993
Solar Energy – Active	994
Solar Energy – Passive	995
Solar Furnace	996
Solar Furnace – The Sun	997
Solar Pond	998
Solar Power	998
Solar Tower	999
Solid Bed Adsorption	999
Solid Desiccant Dehydration	1000
Solid Emissions	1001
Solid Fuels	1002
Solid Fuels from Waste	1002
Solid Fuels from Wood	1003
Solid Waste	1003
Solvent Extraction	1003

Solvent Precipitation	1004
Sorghum	1004
Sour Gas	1005
Soybeans	1005
SO _x	1006
Specific Gravity	1007
Specific Heat	1008
Spontaneous Combustion	1008
Spontaneous Ignition	1009
Spray Tower	1009
Spreading	1010
Stability and Instability	1010
Stabilization	1011
Stack Gas	1011
Stack Gas Scrubbing	1012
Starch Crops	1012
Starches	1013
Steam-Air Gasifier	1014
Steam Explosion	1014
Steam Gasification	1015
Steam-Methane Reforming	1015
Steam-Naphtha Reforming	1017
Steam Reforming	1017
Steam Regenerative Caustic Treating Process	1018
Steam Turbine	1019
Sterols	1020
Stoker Combustors	1021
Straight Vegetable Oil	1021
Stratosphere	1022
Straw	1022
Stretford Process	1022
Stripping	1023
Sublimation	1024
Sugar Beets	1024
Sugar Cane	1025
Sugar Crops	1025
Sugars and Starch	1026
Sulfa-Check Process	1028
SulfaClean HC Liquid Sweetening Process	1028
Sulfatreat Process	1028
SulFerox Process	1029
Sulfinol Process	1029
Sulfur-Containing Gas Removal	1031
Sulfur Cycle	1033
Sulfur Dioxide	1034
Sulfuric Acid Treating Process	1034
Sun	1034
Sunflowers	1035
Supercritical Fluid	1035
Supercritical Fluid Extraction	1036
Super-Slagging Combustor	1036

Surface Tension	1037
Suspended Particulate Matter	1037
Sustainability	1037
Sweetening Processes	1037
Sweet Potatoes	1039
Switchgrass	1039
Synthesis Gas	1040
Synthesis Gas – Fermentation	1041
Synthesis Gas – Fischer-Tropsch Process	1042
Synthesis Gas – Production	1043
Synthesis Gas – Products	1044
Synthesis Gas – Quality	1046
Synthetic Fuels	1046
Synthetic Fuels – Production	1048
Synthetic Gas	1048
Synthetic Gas – Biogas	1048
Synthetic Gas – Blue Water Gas	1050
Synthetic Gas – Carbureted Water Gas	1050
Synthetic Gas – High Btu Gas	1050
Synthetic Gas – Hydrogen	1051
Synthetic Gas – Landfill Gas	1051
Synthetic Gas – Low-Btu Gas	1052
Synthetic Gas – Medium Btu Gas	1052
Synthetic Gas – Producer Gas	1053
Synthetic Gas – Refuse Gas	1053
Synthetic Gas – Synthesis Gas	1053
Synthetic Gas – Water Gas	1054
Synthetic Gas – Wood Gas	1054
Synthol Process	1054
Syntroleum Process	1055

T	1057
Tail Gas	1057
Tail Gas Cleaning	1057
Tail Gas Cleaning – Beavon Process	1058
Tail Gas Cleaning – Claus Process	1058
Tail Gas Cleaning – SCOT Process	1059
Tall Oil	1059
Tallow	1060
Tar Removal from Gas Streams	1061
Tar Removal from Gas Streams – Physical Methods	1061
Tar Removal from Gas Streams – Thermal Methods	1062
Tar Sand	1063
TEA	1065
Tertiary Biomass Feedstocks	1066
Texaco Gasification Process	1066
Texaco Gasifier	1067
Thermal Conversion	1068
Thermal Cracking	1069
Thermal Decomposition	1069
Thermochemical Platform	1070

Thermosphere	1071
Thiolex/Regen Process	1072
Thiopaq DeSO _x Process	1072
Thiopaq Hydrogen Sulfide Removal	1072
Thorium	1072
Tidal Barrage	1073
Tidal Energy	1073
Tidal Stream Generator	1076
Timber Belts	1076
Timberland	1077
Tires – Devulcanization	1077
Tires - Dry Distillation	1077
Tires – Hydrogenation	1078
Tires – Pyrolysis	1078
Tires – Scrap	1078
Ton, Tonne	1079
Torrefaction	1079
Town Gas	1080
Toxicity Characteristic Leaching Procedure	1080
Trace Element	1080
Transesterification	1081
Transformation in the Environment	1086
Transuranium Elements	1088
Traveling Grate Furnace	1089
Tritium	1089
Troposphere	1090
Tumbling-Bed Gasifier	1091
Turbine	1091
Turbine - Condensing	1091
Turbine – Horizontal and Vertical Axis	1092
Turbine – Impulse	1092
Turbine – Reaction	1092
Turbine – Steam	1093
Turbopause	1093
Two-Stage Gasification	1093

U	1095
U-Gas Process	1095
Ultrafiltration and Microfiltration	1095
Unconventional Gas	1096
Undiscovered Reserves	1096
Unit Process	1097
Unisol Process	1097
Unit Collector	1098
Unproven Reserves	1098
Unsaturated Hydrocarbons	1099
Updraft Combustion	1099
Updraft Gasifier	1099
Upflow Expanded-Bed Reactor	1100
Upper Explosive Limit	1100
Upper Flammability Limit	1102

Uranium	1102
Urban Waste	1102
Urban Waste Briquettes	1103
V	1105
Vapor Density	1105
Vapor Pressure	1105
Vegetable Oils	1106
Volatile Matter	1107
Volatile Organic Compounds	1108
Volatility, Flammability, and Explosive Properties	1110
W	1111
Walker Circulation	1111
Waste	1111
Waste Biomass	1113
Waste – Domestic and Industrial	1114
Waste – Effects of	1114
Waste – Fuels From	1116
Waste – Hazardous	1127
Waste to Energy	1128
Waste – Toxicity	1129
Waste – Types	1130
Waste Disposal	1132
Waste Disposal – Acid Hydrolysis	1132
Waste Disposal – Anaerobic Digestion	1133
Waste Disposal – Briquetting	1135
Waste Disposal – Enzymatic Hydrolysis	1135
Waste Disposal – Gasification	1136
Waste Disposal – Incineration	1138
Waste Disposal – Pyrolysis	1140
Waste Management	1142
Waste Management – Biological Methods	1143
Waste Management – Chemical Methods	1146
Waste Management – Physical Methods	1147
Waste Management – Pretreatment	1148
Waste Management – Thermal Methods	1148
Waste Management – Waste Exchange	1150
Waste Minimization and Separation	1151
Waste Streams	1152
Waste Tires	1152
Waste Vegetable Oil	1152
Water	1153
Water-Cooled Vibrating Grate Boiler	1157
Water Cycle	1157
Water Cycle	1158
Water Gas	1159
Water-Gas Shift Reaction	1159
Water Pollutants	1160
Water Pollution	1161
Water Removal from Gas Streams	1161
Water Removal from Gas Streams – Absorption	1163

Water Removal from Gas Streams – Adsorption	1164
Water Removal from Gas Streams – Cryogenics	1165
Water Removal from Gas Streams – Methanol-Based Processes	1165
Water System	1166
Water Washing	1167
Wave Energy	1167
Weibull Distribution	1168
Wellman-Galusha Process	1168
Wellman-Lord Process	1169
Wet Air Oxidation	1170
Wet Gas	1170
Wet Milling Process	1171
Wet Oxidation Processes	1172
Wet Scrubbers	1173
Wet Scrubbing Systems	1173
Wet Sulfuric Acid Process	1173
Wheat Straw	1174
Willow	1174
Wind Energy	1175
Wind Power	1176
Wind Speed and Wind Gusts	1177
Wind Turbines	1177
Wind Turbines – Classification	1180
Wind Turbines – Environmental Impact	1181
Winkler Gasifier	1181
Winkler Process	1182
Wobbe index	1182
Wood	1183
Wood – Biomass	1186
Wood Chips	1188
Wood – Combustion	1189
Wood – Composition and Properties	1190
Wood – Fuels from	1190
Wood Gasification	1191
Wood – Hardwood	1191
Wood Pellets	1192
Wood Powder and Sawdust	1192
Wood – Softwood	1192
Wood – Solvent Extractable Material	1193
Wood – Thermal Treatment	1195
Wood – Uses	1195
Woodall-Duckham Process	1196
Wood Gas	1197
Wood Smoke	1197
Woody Feedstock	1198

X	1199
Xylan	1199
Xylene	1199
Xylose	1200
Xylose Fermentation	1201

Y	1203
Yeast	1203
Yellow Cake	1204
Yellow Flax	1204
Yellow Grease	1204
Z	1207
Zeolite	1207
Zinc Oxide Process	1208
Zinc Oxide Slurry Process	1208
Conversion Factors	1211
Further Reading	1213
About the Author	1215

Introduction

Energy (from whatever the sources – fossil fuel sources or renewable sources, often referred to as alternate sources) appears in many different forms, including electricity, light, heat, chemical energy, and motional (or kinetic) energy. An important scientific discovery in the 19th century was that energy is conserved, which means that energy can be converted from one form to another but that the total amount of energy must stay the same.

Renewable energy can be derived from a variety of sources because the sources can be used and replaced without irreversibly depleting reserves or the sources (such as power from water systems, wind systems, and the sun) are consistently present in the Earth system, which makes these sources a valuable resource for the consistent production of energy. For this reason, renewable sources will continue to grow in importance as replacements for fossil materials used as fuels and as feedstocks for a range of products. Some renewable materials also have particular unique and beneficial properties which can be exploited in a range of products including pharmaceuticals and lubricants.

The concept is centered around a long-term vision that a significant proportion of the demand for energy and raw materials should be met through the commercial exploitation of science from crops, in a way which stimulates biodiversity and reduces greenhouse gas emissions and waste – particularly biodegradable waste going to a landfill site – and slows depletion of finite natural resources.

Fuels based on natural gas and crude oil are well-established products that have served industrial and domestic consumers for more than a hundred years. For the foreseeable future most of these fuels will still be largely based on liquid hydrocarbon derivatives. The specifications of such fuels will, however, continue to be adjusted as they have been and are still being adjusted to meet changing demands from consumers. Traditional refining of natural gas and crude oil underwent increasing levels of sophistication to produce fuels of appropriate specifications. Increasing operating costs continuously put pressure on refining margins but it remains problematic to convert all refinery streams into products with acceptable specifications at a reasonable return.

However, time is running out and natural gas and crude oil, once considered inexhaustible, is now being depleted at a rapid rate – the gas and oil from tight formations notwithstanding. As the amount of available natural gas and crude oil decreases, the need for alternate technologies to produce liquid fuels that could potentially help prolong the liquid fuels culture and mitigate the forthcoming effects of the shortage of transportation fuels that has been suggested to occur under the Hubbert peak oil theory. To mitigate the influence of the oil peak and the subsequent depletion of supplies, unconventional (or non-gas and crude oil) fuels are becoming a major issue in the consciousness of oil-importing countries.

In the near term, the ability of conventional fuel sources and technologies to support the global demand for energy will depend on how efficiently the energy sector can match available energy resources with the end user and how efficiently and cost effectively the energy can be delivered. These factors are related to the continuing evolution of a truly global energy market. In the long term, a sustainable energy future cannot be created by treating energy as an independent topic (Zatzman, 2012). Rather, the role of the energy and the interrelationship of the energy market with other markets and the various aspects of market infrastructure demand further attention and consideration. Greater energy efficiency will depend on the developing world market's ability to integrate energy resources within a common structure.

However, the production of liquid fuels from sources other than natural gas crude oil (as well as coal and oil shale) has a checkered history. The on-again-off-again efforts that are the result of political maneuvering has seen to it that the race to secure self-sufficiency by the production of non-conventional fuels has never got much further than the starting gate! This is due in no small part to the price fluctuations in the price of natural gas and crude oil

accompanied by the lack of foresight by various levels of government. It must be realized that for decades the price of natural gas and crude oil (and the resulting fuel products) has always been maintained at a level that was sufficiently low to discourage the establishment of an alternate fuels industry. However, it is close to the time when the lack of preparedness for the production of non-conventional fuels may set any national government on its heels.

On the other hand, alternate fuels, such as gasoline and diesel fuel derived from non-fossil carbonaceous sources, are making headway into the fuel balance. For example, naphtha – the typical starting liquid for automotive fuels – and biodiesel from plant sources is similar to naphtha and kerosene but may have differences that include a different distribution of the constituents. At this time, the potential for liquid fuels from various types of biomass is also seeing considerable interest.

Whatever the source of the fuels (gaseous, liquid, or solid) there is always the need for methods by which the fuels can be analyzed and specification derived. Typically, this aspect of non-fossil fuel technology is often omitted from many of the relevant works. In order to combat and mitigate such omissions, this encyclopedia contains articles related to product analysis that includes general descriptions of and references to the relevant test methods.

In order to satisfy specific needs with regard to the type of feedstock to be processed, as well as to the nature of the product, the various standard test methods and specifications are a means of describing and/or recommending the rules and conditions for how materials and products should be manufactured, defined, measured, or tested. There are various standards organizations, such as the ASTM International (formerly known as American Society for Testing and Materials). Thus, it is appropriate that in any discussion of the physical properties of fuels from non-fossil fuel sources and, accordingly, where appropriate, the various ASTM test numbers have been cited in the text.

However, although not mentioned in the text, several other countries have standard test methods for fuel identification – examples are Germany (identified by the prefix DIN), the European countries (intended to be used in the European Union and identified by the prefix EN), the International Standards Organization (identified by the prefix ISO) and the United Kingdom (identified by the prefix IP and the prefix BS) – these test methods are not referenced in this encyclopedia but are available through the use of an internet search engine to which the reader is referred for further details and comparison of the test methods.

Following nomenclature and definitions presented in the United States Energy Policy Act of 1992 (Section 301), in the context of the present book, alternate fuels (alternative fuels) are defined as

Methanol, denatured ethanol, and other alcohols; mixtures containing 85 percent or more (or such other percentage, but not less than 70 percent, as determined by the Secretary, by rule, to provide for requirements relating to cold start, safety, or vehicle functions) by volume of methanol, denatured ethanol, and other alcohols with gasoline or other fuels; natural gas; liquefied petroleum gas; hydrogen; coal-derived liquid fuels; fuels (other than alcohol) derived from biological materials; electricity (including electricity from solar energy); and any other fuel the Secretary determines, by rule, is substantially not natural gas or crude oil and would yield substantial energy security benefits and substantial environmental benefits.

It is this definition that is used to guide the contents of this book and show that sources that are “*substantially not petroleum*” are available as sources of fuels.

However, it must be recognized that the forms of energy from renewable sources vary according to the source. For example, biomass and waste can be combusted directly or they can be converted to gaseous fuels and liquid fuels by conversion and refining of the gases and the liquids. The encyclopedia would be missing important articles if there was not some mention of the methods and processes by which gases and liquid products from renewable sources can be prepared for sales. Accordingly, the technologies for refining the gases and liquids into usable fuels and other (petrochemical-type) products are derived from the current natural gas industry and the crude oil industry. Hence the reason for inserting the relevant refining-related articles into the encyclopedia.

In addition, there is a fundamental attractiveness about harnessing such forces in an age which is very conscious of the environmental effects of burning fossil fuels, and where sustainability is an ethical norm. Currently, the focus of many countries is on both adequacy of energy supply long term and also the environmental implications of particular sources. In that regard the near certainty of costs being imposed on carbon dioxide emissions in developed countries at least has profoundly changed the economic outlook of clean energy sources.

However, there is the need to understand that all energy sources have some impact on the environment. Renewable energy sources do substantially less harm to the environment than do fossil fuels (coal, natural gas, and crude oil) by most measures, including air and water pollution, damage to public health, wildlife and habitat loss, water use, land use, and global warming emissions. However, renewables such as biomass as well as sources such as wind, solar, geothermal, and hydropower also have environmental impacts, some of which are significant and must not be ignored. This encyclopedia also presents information related to those aspects of environmental science and engineering that are susceptible to changes caused by renewable energy sources in addition to the environmental effects caused by the use of fossil fuels. It is for these reasons that articles related to the discharge of pollutants into the environment are included.

In fact, when the benefits of developing renewable energy sources are considered, it is equally important to acknowledge that there can also be disadvantages. While all renewable energy sources – wind, solar, geothermal, hydroelectric, and biomass – can provide substantial benefits for the climate and the economy, all energy sources have some impact on the environment and even renewable sources such as biomass, wind, solar, geothermal, biomass, and hydropower also have environmental impacts, some of which are significant. The exact type and intensity of environmental impacts varies depending on the specific technology used, the geographic location, and a number of other factors. By understanding the current and potential environmental issues associated with each renewable energy source, effective measures can be taken to avoid or minimize these impacts as they become a larger portion of the electric supply.

However, there is a variety of environmental impacts associated with the use of alternative energy sources which can include land use and habitat loss, water use that should be recognized and mitigated. They include land use issues and challenges to wildlife and habitat. The exact type and intensity of environmental impacts varies depending on the specific technology used, the geographic location, and a number of other factors. For example, sources of biomass resources for producing energy are diverse, ranging from energy crops (like switchgrass), to agricultural waste, manure, forest products and waste, and urban waste. Both the type of feedstock and the manner in which it is developed and harvested significantly affect land use and life-cycle global warming emissions impacts of producing power from biomass.

It must be realized that the transfer from non-renewable energy source to renewable energy sources is not without some risk. Just as chemicals from non-renewable energy sources can enter the environment, chemicals from renewable energy sources can also enter the air, water, and soil when they are produced, used, or disposed. The impact of these chemicals on the environment is determined by the amount of the chemical that is released, the type and concentration of the chemical, and where it is found. Some chemicals can be harmful if released to the environment even when there is not an immediate, visible impact. On the other hand, some chemicals are of concern as they can work their way into the food chain and accumulate and/or persist in the environment for many years.

The final concentration of a chemical (or a mixture of chemicals) in various environmental systems (such as the atmosphere, water, and the land) depends on environmental emission rates and environmental distribution and fate of the chemical. Thus the first step in environmental risk assessment is always to quantify the emissions of a chemical into the atmosphere, the water, and the land.

Many chemicals, in fact all chemicals, that enter the environment should be categorized and ranked using hazard assessment criteria. This would not only ensure that truly pressing environmental issues are identified and prioritized, but would also maximize the use of limited resources. In the case of soluble chemicals, surrogate data such as persistence and bioaccumulation have been used, in combination with toxicity, for the purpose of hazard categorization. However, for insoluble or sparingly soluble chemicals such as metals and metal compounds, persistence and bioaccumulation are neither appropriate nor useful. Unfortunately, this is not always recognized by regulators or even by scientists.

The use of persistent, bioaccumulative and toxic (PBT) criteria for chemicals was developed to address the hazards posed by synthetic organic chemicals. In fact, the criteria and test methods to evaluate persistence (i.e., the lack of degradability of a chemical) and bioaccumulation (the dispersion of a chemical through knowledge of the water-octanol partition coefficient) were developed to be used in combination with toxicity in order to reduce the importance given to the use of toxicity data alone. These test methods were based on an understanding of the chemistry of chemicals of concern at the time and of the biological interactions that the chemicals would have with the surrounding

biota. Specifically, it was realized that if some chemicals exerted high intrinsic toxicity under standardized laboratory test conditions but did not persist or bioaccumulate, the environmental hazard of such chemicals would be lower.

As mentioned above, persistence is measured by determining the lack of degradability of a substance from a form that is biologically available and active to a form that is less available. This applies to many substances – metals and metal compounds tend to be in forms that are not bioavailable. Only under specific conditions would metals or metal compounds transform into a bioavailable form. Thus, rather than persistence, the key criterion for classifying metals and metal compounds should be their capacity to transform into bioavailable form(s). Furthermore, although bioavailability is a necessary precursor to toxicity, it does not inevitably lead to toxicity. Although metals and metal compounds stay in the environment for long periods of time, the risk they may pose generally decreases over time. For example, metals introduced into the aquatic environment are subject to removal/immobilization processes (e.g., precipitation, complexation and absorption).

Similarly, the use of bioaccumulation has significant limitations for predicting hazard for metals and metal compounds. Generally, either bioconcentration factors (BCFs) or bioaccumulation factors (BAFs) are used for this purpose. A bioconcentration factor is the ratio of the concentration of a substance in an organism, following direct uptake from the surrounding environment (water), to the concentration of the same substance in the surrounding environment. A bioaccumulation factor considers uptake from food as well. In contrast to organic compounds, uptake of metals is not based on lipid partitioning. Further, organisms have internal mechanisms (homeostasis) that allow them to regulate (bioregulate) the uptake of essential metals and to control the presence of other metals. Thus, if the concentration of an essential metal in the surrounding environment is low and the organism requires more, it will actively accumulate that metal. This will result in an elevated bioconcentration factors (or bioaccumulation factor) value which, while of concern in the case of organic substances, is not an appropriate measure in the case of metals.

The primary determining factor of hazard for metals and metal compounds is therefore toxicity, which requires consideration of dose (indeed, the fundamental tenet of toxicology is *the dose makes the poison*). Historically, it has been the practice to measure the toxicity of soluble metal salts, or indeed the toxicity of the free metal ion. However, in different media, metal ions compete with different types or forms of organic matter (e.g., fish gills, suspended solids, soil particulate material) to reduce the total amount of metals present in bioavailable form. Toxicity of the bioavailable fraction (i.e., as determined through transformation processes) is the most appropriate and technically defensible method for categorizing and ranking the hazard of metals and metal compounds.

The relative proportion of hazardous constituents present in any collection of chemicals (crude oil-derived products included) is variable and rarely consistent because of site differences. Therefore, the extent of the contamination will vary from one site to another and, in addition, the farther a contaminant progresses from low molecular weight to high molecular weight the greater the occurrence of polynuclear aromatic hydrocarbons, complex ring systems (not necessarily aromatic ring systems) as well as an increase in the composition of the semi-volatile chemicals or the non-volatile chemicals. These latter chemical constituents (many of which are not so immediately toxic as the volatiles) can result in long-term/chronic impacts to the flora and fauna of the environment. Thus, any complex mixture of chemicals should be analyzed for the semi-volatile compounds which may pose the greatest long-term risk to the environment.

Heavy metals are common chemical pollutants. The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg. Those metals are important since they are capable of decreasing crop production due to the risk of bioaccumulation and biomagnification in the food chain. There is also the risk of superficial and groundwater contamination. Knowledge of the basic chemistry, environmental, and associated health effects of these heavy metals is necessary in understanding their speciation, bioavailability, and remedial options. The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana et al., 2001). This distribution is believed to be controlled by reactions of heavy metals in soils such as (i) mineral precipitation and dissolution, (ii) ion exchange, adsorption, and desorption, (iii) aqueous complexation, (iv) biological immobilization and mobilization, and (v) plant uptake (Levy et al., 1992). The toxicity of metals varies greatly with pH, water hardness, dissolved oxygen levels, salinity, temperature and other parameters.

The specific type of metal contamination found in a contaminated soil is related to the operation that occurred at the site. The range of contaminant concentrations and the physical and chemical forms of contaminants will also depend on activities and disposal patterns for contaminated wastes on the site. Other factors that may influence the form, concentration, and distribution of metal contaminants include soil and groundwater chemistry and local transport mechanisms.

Finally, in order to evaluate the impact of a chemical that has been released to the environment, the chemical must be characterized in terms of the transport and transformation in that system (atmosphere, water, or land) and the potential for the transport of the chemical from one system to another or from one system to the other two. The assessment should focus on areas with which a released chemical is most likely to have contact. For a meaningful characterization, the environment must be viewed as a series of interacting compartments and it must be determined whether a chemical will remain and accumulate in the local area of the origin of the chemical. The potential for the chemical to be physically, chemically, or biologically transformed in the system of its origin (such as by hydrolysis, oxidation, or other transformation; Chapter 8) or be transported to another system such as by volatilization or by precipitation. The chemical could also be transferred by deposition and runoff to surface water that provides drinking water.

Each of these scenarios defines a pathway from the air emission to contact with a person, and each pathway has an associated route of contact. The true potential for exposure cannot be quantified until the pathways and routes that account for a substantial fraction of the intake and uptake for the receptor population have been identified. The likelihood of any pathway depends on the chemical properties of the substance released, where and how it is released, and environmental conditions. Sometimes the exposure increases along a pathway (such as bioaccumulation), but more often the exposure may decrease.

Thus, characterizing transportation pathways begins at the source of the agent release. In some situations, the source may be obvious and can be defined and characterized from air or soil concentrations. In many cases, such as contamination of water supplies, sources and emissions may be multiple and poorly characterized. However, classification of a potential transportation route should, as much as possible, be based on the released volume, duration of the release, and the rate of emission.

In order to fully understand the impact of a released chemical on the environment, the potential for chemical transformation of the spilled chemical which may occur as a result of biotic or abiotic processes, can significantly reduce the concentration of a substance or alter its structure in such a way as to enhance or diminish its toxicity or change its toxic effect. For example, for many airborne organic compounds, transformation processes, such as photolytic decomposition and oxidation/reduction reactions, can result in conversion to other compounds. For organic chemicals, the half-life of the chemical for any given transformation process provides a useful index of persistence in environmental media. For example, the photochemical half-life can vary from day to night, and specific information on the rates and pathways of transformation for individual chemicals of concern must be obtained directly from experimental determinations or derived indirectly from information on chemicals that are structurally similar to the released chemical.

Despite these environmental impacts, renewable energy technologies compare extremely favorably to fossil fuels, and remain a core part of the solution to future energy requirements. Renewable energy is going to be an important source for power generation in the near future because the resources again and again produce useful energy. Wind power generation is considered as having lowest water consumption, lowest relative greenhouse gas emission, and most favorable social impacts. It is considered as one of the most sustainable renewable energy sources, followed by hydropower, photovoltaic, and then geothermal. As these resources are considered as clean energy resources, they can be helpful for the mitigation of greenhouse effect and global warming effect.

However, by understanding the components of the environment and the current and potential environmental issues associated with each renewable energy source, the reader can understand the means to effectively avoid or minimize these impacts as they become a larger portion of energy supply. For this reason, this encyclopedia is an all-inclusive work that also presents not only the environmental components but also the various environmental aspects of the generation and use of renewable energy. Other issues arise that are similar to those produced by the use of fossil fuels – contamination of the atmosphere, water, and the land – but the degree of the contamination is not the same.

However, it would be a serious omission if recognition of some of the potential properties and effects of renewable fuels such as biogas and bio-oil and were omitted from this work. For example, biogas and bio-oil could cause harm

to the environment is used without any form of treatment. The gas needs to be cleaned of objectionable environmentally harmful constituents and the bio-oil (from whatever the source) needs to be processed to provide useable products. Accordingly, it has been necessary to include options for gas cleaning and options for bio-oil refining (such as hydrotreating and hydrocracking) so that the reader may understand the conditioning of these products into environmentally benign use.

The dynamics are now coming into place for the establishment of an alternate energy industry and it is up to various levels of government not only to promote the establishment of such an industry but to lead the way, recognizing that it is not only supply and demand but the available and variable technology. The processes for recovery of the raw materials and the processing options have changed in an attempt to increase the efficiency of energy production.

In addition, there are several interrelationships between conventional fuels and alternate fuels, especially in the areas of fuel production and fuel refining. Accordingly, it has been found necessary to include segments for the conventional fuel industries that are applicable to the alternate fuels industries. As ready reference, the articles in this encyclopedia have been assembled to assist the reader to understand the options that are available for the production of alternate energy, especially alternate fuels, and such processes from the conventional fuels industries and also from the unconventional fuels are, where they are applicable to renewable fuels, also included.

The Scrivener Encyclopedia of Renewable Energy was compiled because the need was recognized for an extensive work on the nature of renewable energy sources. This will be a convenient-to-use encyclopedia that will be a suitable companion for the researcher, teacher, and manager. Also, in order for help the reader understand the nature of renewable energy sources (Table 1), the encyclopedia contains segments that will allow the reader to compare renewable energy sources with the (to date) more conventional fossil fuels resources and how the conventional processing units that will be necessary to process renewable energy sources that are in the form of gases, liquid and solid.

Table 1 Simplified categorization and nomenclature of the various energy sources.

<i>Conventional Energy Sources</i> Natural gas Crude oil Heavy crude oil Coal*
<i>Non-conventional Energy Sources</i> Extra heavy crude oil Tar sand bitumen Coal* Coal gas Coal liquids Shale oil
<i>Renewable Energy Sources</i> Biomass Waste Hydrogen Hydroelectric energy** Geothermal energy Nuclear energy Ocean Energy** Solar energy Tidal energy** Wind energy

*When used as a solid fuel for combustion processes and without any modification other than cleaning, coal is often considered to be a conventional energy source.

**Often grouped together under the name “hydrokinetic energy” – hydroelectric energy may also be included in this group.

The encyclopedia also contains a section on further reading for those readers who require further information on any of the subjects.

Finally, the temperature scales used in this work are the Centigrade (Celsius) scale and the Fahrenheit scale. Generally, when the temperature is below 100°C the conversion to the exact temperature in degrees Fahrenheit is presented immediately following in parenthesis. On the other hand, when the temperature is above 100°C the conversion to the nearest 5° Fahrenheit is presented immediately following in parenthesis.

Dr. James Speight
Laramie, Wyoming, USA
February 2021

Absorption

When gaseous products are produced from a source, the gas stream will invariably contain unwanted constituents that must be removed. This not only applies to natural gas streams and gas streams produced during the refining of the crude oil (as well as to gas streams produced from the other fossil fuels) but also to the alternative fuel industry where gas streams are produced from feedstocks such as biomass and waste. One such process for removing the unwanted constituents is the absorption process.

Absorption is a physical or chemical process by which molecules enter a liquid or solid bulk phase and is different to adsorption in which a chemical is subject to the surface forces of the adsorbent (Table A-1).

Table A-1 Examples of the types of absorption.

Solute*	Absorbent	Absorption type
Ammonia	Water	Physical
Carbon dioxide	Ethanolamine	Chemical, reversible
Carbon dioxide	Sodium hydroxide (aq.)	Chemical, irreversible
Hydrochloric acid	Sodium hydroxide (aq.)	Chemical, irreversible
Hydrochloric acid	Water	Physical
Hydrogen sulfide	Sodium hydroxide (aq.)	Chemical, irreversible
Hydrogen sulfide	Olamine**	Chemical, reversible
Nitrogen oxides	Water	Chemical, reversible
Sulfur dioxide	Water	Physical and chemical***

*Listed alphabetically by solute.

**For example, monoethanolamine and diethanolamine.

***In addition to dissolution (physical absorption), there is also the potential for chemical absorption by the occurrence of the reversible reaction: $\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_3$

Absorption is the process by which a gas is distributed throughout an absorbent (liquid); depends only on physical solubility and may include chemical reactions in the liquid phase (chemisorption). The process is generally used to separate a higher-boiling constituent from other components of a system of vapors and gases. The absorption medium is usually an oil in the range of gas oil. Absorption is widely employed in the gas clearing (gads processing) industry for recovery or removal of constituents from natural gas stream and from cured oil refinery streams of natural gasoline from well gas and of vapors given off by storage tanks. The reverse of this, i.e., the transfer of the absorbed constituents (the stripping process) is accomplished by contacting the absorbent (liquid or solid) liquid with an inert gas such as nitrogen or steam. With aqueous waste streams the stripping gas is usually air.

Scrubbing is primarily concerned with the removal of particulate liquids or solids from gas streams by contacting the gas with a liquid scrubbing medium. That is, the particles are scrubbed out of the gas. However, if the gas also contains some soluble gaseous components, they can dissolve in the scrubber solution. Thus, the scrubber may also be an absorber, just as an absorber may also be a scrubber if the feed contains particulate matter as well as soluble components. Absorption and scrubbing are commonly used separation processes for preventing air pollution from industrial exhaust or stack gases. Stripping is used for both prevention of water pollution by treatment of wastewaters to remove soluble toxic gases and remediation of contaminated water at already existing hazardous waste sites.

Typically, absorption is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon) and is different from adsorption (Table A-2).

Table A-2 Comparison of adsorption and absorption.

	Adsorption	Absorption
Definition	Accumulation at the surface the solid or liquid	Accumulation in the bulk of solid or liquid
Characteristic	A surface phenomenon	A bulk phenomenon
Concentration	Different at surface to bulk	Same throughout
Reaction rate	Increases to equilibrium	Occurs at a uniform rate
Reaction type	Exothermic process	Endothermic process
Temperature	Unaffected by temperature	Not affected by temperature

Chemical adsorption processes adsorb sulfur dioxide onto a carbon surface where it is oxidized (by oxygen in the flue gas) and absorbs moisture to give sulfuric acid impregnated into and on the adsorbent.

Liquid absorption processes (which usually employ temperatures below 50°C (120°F) are classified either as physical solvent processes or chemical solvent processes. The former processes employ an organic solvent, and low temperatures, or high pressure, or both enhance absorption; regeneration of the solvent is often accomplished readily. In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkaline solutions such as amines or carbonates. Regeneration (desorption) can be achieved by the use of reduced pressures and/or high temperatures, whereby the acid gases are stripped from the solvent.

If absorption is a physical process not accompanied by any other physical or chemical process, it usually follows the Nernst partition law in which the ratio of concentrations of solute species in two bulk phases in contact is constant for a given solute and bulk phases, i.e.:

$$X_1/X_2 = \text{constants} = K_{N(X\ 1,2)}$$

The value of constant K_N , the *partition coefficient*, is dependent upon temperature and the value is valid if concentrations are not too large and if the species x does not change its chemical or physical form in either phase-1 or phase-2.

In the case of gas absorption, the concentration a solute (c) in one of the phases can be calculated using the *Ideal gas law* (e.g., $c = p/RT$). Alternatively, partial pressure may be used instead of concentration.

The absorption oil has an affinity for the natural gasoline constituents. As the gas stream is passed through an absorption tower, it is brought into contact with the (lean) absorption oil which soaks up a high proportion of the liquid hydrocarbons. The rich absorption oil now containing the hydrocarbons exits the absorption tower through the base after which it is fed into lean oil stills, where the mixture is heated to a temperature above the boiling point of the absorbed hydrocarbons but below that of the oil. This process allows for the recovery of approximately 75% v/v of butanes, and 85 to 90% v/v percent of pentanes and higher boiling hydrocarbons from the stream.

The process above can be modified to improve its effectiveness, or to target the extraction of specific hydrocarbons. In the refrigerated oil absorption method, where the lean oil is cooled through refrigeration, propane recovery can be upwards of 90% v/v and around 40% v/v of any of ethane present in the gas stream. Extraction of higher molecular weight hydrocarbons approaches 100% v/v using this process.

See also: Adsorption, Gas Cleaning, Gas Processing, Gas Treating.

Absorption Cleaning

Absorption is an approach in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). Gas absorption (sometimes also known as gas scrubbing) is an operation in which a gas mixture is contacted with a

liquid for the purpose of preferentially dissolving one or more components of the gas mixture and to provide a solution of the components in the liquid phase. When water and hydrocarbon oils are used as absorbents, no significant chemical reactions occur between the absorbent and the solute, and the process is commonly referred to as physical absorption.

The process involves a mass transfer of the component of the gas from the gas phase to the liquid phase in which the solute so transferred is absorbed by the liquid. In gas desorption (also known as stripping), the mass transfer is in the opposite direction, i.e., from the liquid phase to the gas phase. Typically, there is no chemical reaction involved in the absorption process and it operates under isothermal conditions. Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, the gas-liquid contactor designs which are employed are plate columns or packed beds.

Chemical adsorption processes adsorb sulfur dioxide onto a carbon surface where it is oxidized (by oxygen in the flue gas) and absorbs moisture to give sulfuric acid impregnated into and on the adsorbent. When aqueous sodium hydroxide (a strong base) is used as the absorbent to dissolve an acid gas, absorption is accompanied by a rapid and irreversible neutralization reaction in the liquid phase and the process is referred to as chemical absorption or reactive absorption.

More complex examples of chemical absorption are processes for acid gas removal from gas streams. In the process, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are absorbed by treating the gas stream (invariably by passing the gas stream through the liquid absorbent) with an aqueous solution of monoethanolamine (MEA), diethanolamine (DEA), diethylene glycol (DEG) or triethylene glycol (TEG), where a reversible chemical reaction takes place in the liquid phase. Chemical reactions can increase the rate of absorption, increase the absorption capacity of the solvent, increase selectivity to preferentially dissolve only certain components of the gas, and convert a hazardous chemical to a safe compound.

See also: Absorption, Gas Cleaning, Gas Processing, Gas Treating, Scrubbing, Stripping.

Absorption Dehydration

An example of absorption dehydration is known as *glycol dehydration* and diethylene glycol, the principal agent in this process, has a chemical affinity for water and removes water from the gas stream. In this process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream.

Essentially, glycol dehydration involves using a glycol solution, usually either diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in a *contactor*. The glycol solution will absorb water from the wet gas and once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The gas stream, having been stripped of most of its water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the gas stream, is put through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100°C , 212°F) and glycol (204°C , 400°F) makes it relatively easy to remove water from the glycol solution, allowing it to be reused in the dehydration process.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In the past, this methane was simply vented out of the boiler. In addition to losing a portion of the gas stream that was extracted, this venting contributes to air pollution and the greenhouse effect. In order to decrease the amount of methane and other compounds that are lost, flash tank separator-condensers work to remove these compounds before the glycol solution reaches the boiler. Essentially, a flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbons to vaporize (*flash*).

The glycol solution then travels to the boiler, which may also be fitted with air or water cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas (e.g., heavy hydrocarbon vapors, the *Drizo process*) or vacuum distillation are recommended.

In practice, absorption systems recover 90 to 99% by volume of methane that would otherwise be flared into the atmosphere.

See also: Absorption, Gas Cleaning, Gas Processing, Gas Treating.

Absorption Oil

Absorption oil (also called absorber oil, scrubbing oil, wash oil) is low-boiling liquid hydrocarbon used to absorb or remove the higher-boiling liquid hydrocarbons from a gas stream. Typically, absorption oil is a hydrocarbon-based liquid that is contacted with a gas stream to remove higher boiling components, such as occurs in the recovery of natural gasoline from the gas stream (often referred to as the wet gas stream).

An absorption plant is a facility used to recover the condensable portion of the gas stream to remove acid gas stream. Typically, the absorption takes place in a counter-flow (countercurrent) vessel, where the gas stream enters the bottom of the vessel and flows upward through the absorption oil. The plant also includes the necessary ancillary thermal units to distill the absorbed hydrocarbons from the higher boiling absorption oil.

See also: Absorption, Absorption Processes, Gas Cleaning, Gas Processing, Gas Treating, Olamine Processes.

Absorption Process

The absorption method of extraction is similar to using absorption for dehydration. The main difference is that in the absorption of liquids from the gas stream, absorbing oil is used as opposed to glycol. This absorbing oil has an affinity for gas liquids in much the same manner as glycol has an affinity for water. Before the oil has picked up any gas stream liquids, it is termed lean absorption oil.

The oil absorption process involves the countercurrent contact of the lean (or stripped) oil with the incoming wet gas with the temperature and pressure conditions programmed to maximize the dissolution of the liquefiable components in the oil. The rich absorption oil (sometimes referred to as fat oil), containing gas liquids, exits the absorption tower through the bottom. It is now a mixture of absorption oil, propane, butanes, pentanes, and other higher-boiling hydrocarbons. The rich oil is fed into lean oil stills, where the mixture is heated to a temperature above the boiling point of the gas liquids but below that of the oil. This process allows for the recovery of around 75% by volume of the butane derivatives, and 85 to 90% by volume of the pentane derivatives, and higher-boiling constituents from the gas stream.

The basic absorption process above can be modified to improve its effectiveness, or to target the extraction of specific gas stream liquids. In the refrigerated oil absorption method, where the lean oil is cooled through refrigeration, propane recovery can be upwards of 90% by volume, and approximately 40% by volume of the ethane can be extracted from the gas stream. Extraction of the other, higher-boiling liquids can be close to 100% by volume using this process.

The absorption method, on the other hand, uses an absorbing oil to separate the methane from the gas stream liquids. While the gas stream is passed through an absorption tower, the absorption oil (lean oil) soaks up a large amount of the gas liquids. The absorption oil (enriched oil), now containing gas liquids, exits the base of the tower after which the enriched oil is fed into distillers where the blend is heated to above the boiling point of the gas liquids, while the oil remains fluid. The absorption oil is recycled while the gas liquids are cooled and directed to a fractionator tower. Another absorption method that is often used is the refrigerated oil absorption method where the lean oil is chilled rather than heated, a feature that has the potential to enhance recovery rates.

More specifically, to allow the process to operate at low temperatures, the feed gas must be injected with ethylene glycol solution to avoid hydrate formation in the heat exchangers. The feedstock (the gas stream) is cooled by propane refrigeration and separated in a cold separator, typically at approximately -18°C (0°F). The separator liquid is sent to the ethane recovery unit (the deethanizer) while the separator vapor is routed to the absorber operating at 400 psig. Refrigerated lean oil is used to absorb the higher molecular weight hydrocarbons (the C3+ constituents) from the gas stream thereby producing a lean gas and a propane rich bottom which is sent to the deethanizer. The deethanizer operates at a lower pressure, typically at 200 psig, producing an ethane rich gas and a rich oil bottom containing the C3+ components.

The overhead stream from the deethanizer is compressed to the sales gas pipeline or used as fuel gas. The bottom product is further processed in a rich oil still which regenerates a lean oil to be recycled back to the absorber and an overhead distillate containing the C3+ constituents. The C3+ stream can be fractionated in a propane recovery unit (the depropanizer) which produces the propane and butane product. Because of the high-boiling material of the lean oil, a heater is used in the rich oil still. If necessary, the lean oil composition can be controlled using a lean oil still (not shown) to remove the heavy tails of the lean oil from the process.

See also: Absorption, Gas Cleaning, Gas Processing, Gas Treating.

Absorption Tower

An absorption tower (also known as a scrubbing tower) is a long vertical column that typically contains packed bed which is used for absorbing gases from gas streams. The gas is introduced at the bottom of the column and the absorbing liquid, often water, passes in at the top and falls down against the countercurrent of gas. In the tower, the higher-boiling (gasoline-range) hydrocarbon derivatives are partially absorbed by a liquid in the form of falling droplets.

The gas stream is introduced into the lower portion of the tower and flows upwards while making contact with a washing fluid. The tower is provided with one or several washing stages, each comprising one or several venturi tubes through which the gas is given a speed increase and the washing fluid is discharged through fluid nozzles in the gas flow path. Liquid distribution in the tower occurs in the gas flow in directions forming such angles to the vertical that the fluid flow will not fall backwards and it is preferential that the gas flow is not interrupted.

There are many devices that fall into the category of absorption tower – packed towers (packed columns) are most frequently used to remove contaminants from a gas stream. However, packed towers can also be used to remove volatile components from a liquid stream by contacting it with an inert gas (stripping). They are also used in distillation applications where the separation is particularly difficult due to close boiling components.

The packed tower consists of a vertical hollow column that is filled with small solid pieces (the packing) which occupy the space but leave voids between the pieces. Thus a liquid stream can be introduced into the top of the tower and flow down over the surface of the pieces, creating a large surface area for a given volume of liquid. The gas to be treated is introduced into the tower and flows through the voids where it comes into intimate contact with the surface of the liquid. The packings are divided into three principal types: (i) dumped packings, which is the loose packing method, (ii) stacked packings, which is the dense packing method, and (iii) structured packing, which is the ordered packing method.

The diameter of a packed absorption tower depends on the quantities of gas and liquid handled, their properties, and the ratio of one stream to the other. The height of the tower, and hence the total volume of packing, depends on the magnitude of the desired concentration changes and on the rate of mass transfer per unit of packed volume.

See also: Absorption Oil, Gas Cleaning, Gas Processing, Gas Treating.

Accuracy and Precision in Analysis

Analysis is the means by which any fuel (fossil or alternative, especially a biomass-derived) fuel is characterized and accuracy and precision are required otherwise the analytical data are suspect and cannot be used with any degree of certainty. This is also especially true of analytical data that is reused for commercial operations where the fuel may be sold on the basis of heat content.

Thus, the *accuracy* of a test is a measure of how close the test result will be to the true value of the property being measured. As such the accuracy can be expressed as the *bias* between the test result and the true value. However, the *absolute accuracy* can only be established if the true value is known. In the simplest sense, a convenient method to determine a relationship between two measured properties is to plot one against the other. Such an exercise will provide either a line fit of the points or a spread that may or may not be within the limits of experimental error. The data can then be used to determine the approximate accuracy of one or more points employed in the plot. For example,

a point that lies outside the limits of experimental error (a *flyer*) will indicate an issue of accuracy with that test and the need for a repeat determination.

However, the graphical approach is not appropriate for finding the absolute accuracy between more than two properties. The well-established statistical technique of regression analysis is more pertinent to determining the accuracy of points derived from one property and any number of other properties. There are many instances in which relationships of this sort enable properties to be predicted from other measured properties with as good precision as they can be measured by a single test. It would be possible to examine in this way the relationships between all the specified properties of a product and to establish certain key properties from which the remainder could be predicted, but this would be a tedious task.

An alternative approach to that of picking out the essential tests in a specification using regression analysis is to take a look at the specification as a whole, and extract the essential features (termed *principal components analysis*).

Principal components analysis involves an examination of set of data as points in n -dimensional space (corresponding to a number (n) of original tests) and determines (first) the direction that accounts for the biggest variability in the data (*first principal component*). The process is repeated until n principal components are evaluated, but not all of these are of practical importance since some may be attributable purely to experimental error. The number of significant principal components shows the number of independent properties being measured by the tests considered.

Following from this, it is necessary to establish the number of independent properties that are necessary to predict product performance in service with the goals of rendering any specification more meaningful and allowing a high degree of predictability of product behavior. On a long-term approach it might be possible to obtain new tests of a fundamental nature to replace, or certainly to supplement, existing tests. In the short term, selecting the best of the existing tests to define product quality is the most beneficial route to predictability.

On the other hand, the *precision* of a test method is the variability between test results obtained on the same material, using a specific test method. The precision of a test is usually unrelated to its accuracy. The results may be precise, but not necessarily accurate. In fact, the precision of an analytical method is the amount of scatter in the results obtained from multiple analyses of a homogeneous sample. To be meaningful, the precision study must be performed using the exact sample and standard preparation procedures that will be used in the final method. Precision is expressed as repeatability and reproducibility.

The *intra-laboratory precision* or the *within-laboratory precision* refers to the precision of a test method when the results are obtained by the same operator in the same laboratory using the same apparatus. In some cases, the precision is applied to data gathered by a different operator in the same laboratory using the same apparatus. Thus, intra-laboratory precision has an expanded meaning insofar as it can be applied to laboratory precision.

Repeatability or repeatability interval of a test (r) is the maximum permissible difference due to test error between two results obtained on the same material in the same laboratory.

$$r = 2.77 \times \text{standard deviation of test}$$

The repeatability interval (r) is, statistically, the 95% probability level or the differences between two test results are unlikely to exceed this repeatability interval more than five times in a hundred.

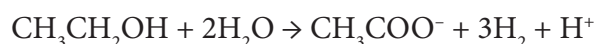
The *inter-laboratory precision* or the *between-laboratory precision* is defined in terms of the variability between test results obtained on the aliquots of the same homogeneous material in different laboratories using the same test method.

The term *reproducibility* or *reproducibility interval* (R) is analogous to the term repeatability but it is the maximum permissible difference between two results obtained on the same material but now in different laboratories. Therefore, differences between two or more laboratories should not exceed the reproducibility interval more than five times in a hundred.

$$R = 2.77 \times \text{standard deviation of test}$$

Acetogenesis

Acetogenesis is the third phase of anaerobic digestion in which simple molecules created through the acidogenesis phase are further digested by acetogens to produce largely acetic acid, as well as carbon dioxide and hydrogen.



The acid-producing bacteria, involved in the second step, convert the intermediates of fermenting bacteria into acetic acid (CH_3COOH), hydrogen (H_2) and carbon dioxide (CO_2). These bacteria are facultatively anaerobic and can grow under acid conditions. To produce acetic acid, the bacteria need oxygen and carbon. For this, they use the oxygen solved in the solution or bounded-oxygen whereby the acid-producing bacteria create an anaerobic condition which is essential for the methane producing microorganisms. Moreover, these bacteria reduce the compounds with a low molecular weight into alcohols, organic acids, amino acids, carbon dioxide, hydrogen sulfide and traces of methane.

From a chemical standpoint, this process is partially endergonic (i.e., only possible with energy input), since bacteria alone are not capable of sustaining that type of reaction. An endergonic reaction is a chemical reaction in which total amount of energy is a loss – it takes more energy to initiate the reaction than the energy produced by the reaction and, thus, the total energy is a negative net result.

An acetogen is a microorganism that generates acetate (CH_3COO^-) as an end product of anaerobic respiration (fermentation) and can produce, in most cases, acetate as the end product) from two molecules of carbon dioxide (CO_2) and four molecules of molecular hydrogen (H_2). This process (acetogenesis) is different from acetate fermentation, although both occur in the absence of molecular oxygen (O_2) and produce acetate. Acetogens are found in a variety of habitats, generally those that are anaerobic (lack oxygen). Thus, acetogenesis is a process through which acetate is produced from carbon dioxide and an electron source (such as hydrogen and carbon monoxide) by anaerobic bacteria. In this reaction, carbon dioxide is reduced to carbon monoxide and formic acid (HCO_2H) or directly into a formyl group, the formyl group is reduced to a methyl group and then combined with the carbon monoxide and Coenzyme A produce acetyl-CoA. Two specific enzymes participate on the carbon monoxide side of the pathway: (i) CO-dehydrogenase, which catalyzes the reduction of the carbon dioxide and (ii) acetyl CoA synthase, which combines the resulting carbon monoxide with a methyl group to give acetyl-CoA.

The key aspects of the acetogenic pathway are several reactions that include the reduction of carbon dioxide to carbon monoxide and the attachment of the carbon monoxide to a methyl group. The first process is catalyzed by specific enzymes (carbon monoxide dehydrogenase enzymes) and the coupling of the methyl group (provided by methylcobalamin) and the carbon monoxide is catalyzed by acetyl CoA synthetase.



The accumulation of hydrogen can inhibit the metabolism of the acetogenic bacteria and present knowledge suggests that hydrogen may be a limiting feedstock for methanogens. This assumption is based on the fact that addition of hydrogen-producing bacteria to the natural biogas-producing consortium increases the daily biogas production. At the end of the degradation chain, two groups of methanogenic bacteria produce methane from acetate or hydrogen and carbon dioxide. These bacteria are strict anaerobes and require a lower redox potential for growth than most other anaerobic bacteria.

See also: Acidogenesis, Anaerobic Digestion, Methanogenesis.

Acid Catalyst

A catalyst alters the rate of a reaction without changing the reaction thermodynamic parameters through another route. Normally, the one in the energy of the transition state is lower. There are two types of catalysts which can affect the reaction pathway: (i) homogeneous catalysis and (ii) heterogeneous catalysts.

Since the acidity of the catalyst support reflects the reaction pathway and plays a key role in the catalyst performance, it is possible to differentiate between homogeneous and heterogeneous catalyst. The homogeneous catalyst has lower ability of acidic sites rather than heterogeneous catalysts and it requires higher temperature in its reaction system, whereas the solid structure and the surface of a heterogeneous catalyst give its ability for higher strength and locations for acidic sites.

Many mineral acid catalysts that are active in homogeneous catalysis can be made suitable for heterogeneous catalysis by supporting the catalyst on an inorganic oxide. Strongly acidic heterogeneous catalysts are prepared by supporting Brønsted acids such as trifluoro-sulfonic acid, sulfuric acid, phosphoric acid, and Lewis acids (such as boron trifluoride, BF_3 , and antimony pentafluoride, SbF_5) on high surface area oxides such as silica, SiO_2 , alumina, Al_2O_3 , and zirconia, ZrO_2). In particular, supported phosphoric acid on silica is still widely used, and $\text{BF}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ and $\text{H}_2\text{SO}_4\text{-ZrO}_2$ possess acidic sites that enable them to perform reactions that other solids are not strong enough acids to catalyze. Supported acids are difficult to characterize and are highly dependent on the methods and materials used in their preparation but do offer a suitable alternative for reactions that require strong and even super acidity.

See also: Catalysts.

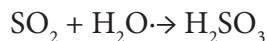
Acid Deposition

Acid deposition is the scientific term used to describe acid rain (which includes including acid fog, acid sleet, and acid snow).

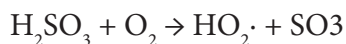
Acid deposition (acid rain) occurs when sulfur dioxide (SO_2) and, to a lesser extent, NO_x emissions are transformed in the atmosphere and return to the earth as dry deposition or in rain, fog, or snow. Acid rain is another environmental problem that affects many industrialized area of the world resulting in damage crops, forests, wildlife populations, and causing respiratory and other illnesses in humans.

When atmospheric pollutants such as sulfur dioxide and nitrogen oxides mix with water vapors in the air, they are converted to sulfuric and nitric acids.

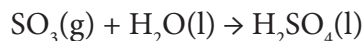
Sulfur dioxide with water in produce sulfurous acid:



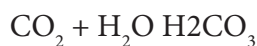
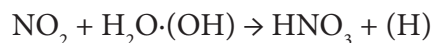
In the gas phase, sulfur dioxide is oxidized by reaction with the hydroxyl radical via an intermolecular reaction:



In the presence of water sulfur trioxide (SO_3) is converted rapidly to sulfuric acid:



Nitric acid is formed by the reaction of water with nitrogen dioxide and by the reaction of carbon dioxide with water:



Although carbonic acid is a weaker acid than nitric acid, sulfurous acid, and sulfuric acid, it does, however, contribute to acid rain which, in high concentrations, can cause damage to natural environments including forests and freshwater lakes.

Acid deposition can be classified as wet deposition such as acid rain, snow, sleet and fog or dry deposition such as deposition as particulate matter even less than $PM_{2.5}$. Effects of acid rain can be either chronic or episodic. Chronic acidification is a long-term effect due to years of acid rain. Episodic acidification is due to heavy rain storms; it also occurs in spring as concentrated nitrate and sulphate in lower layer of snow pack get released when snow melts. A second method of acid deposition is known as dry deposition. Whilst wet deposition involves the precipitation of acids, dry deposition occurs when the acids are first transformed chemically into gases and salts, before falling under the influence of gravity back to Earth. Sulfur dioxide, for example, is deposited as a gas and as a salt.

The gases present in acid deposition are found to occur naturally in the environment. They are given off from a number of sources including volcanic eruptions and the rotting of vegetation. They become a problem when humans produce the gases in large amounts and at high concentrations by the burning of fossil fuels. It is arguable which gives off the most acid gases – fossil fuels or natural events such as eruption of volcanoes. The distances that pollutant gases travel means that acid deposition is an international or trans-boundary problem. This means that acid pollutants are not necessarily deposited in the same country where they were produced.

Acid rain falling over regions with alkaline soils or rocks is quickly neutralized but in areas with little acid-neutralizing capacity is the biosphere sensitive to acid rain. Over North America these areas include New England, eastern Canada, and mountainous regions, which have granitic bedrock and thin soils.

In areas where the biosphere is sensitive to acid rain, there has been ample evidence of the negative effects of acid rain on freshwater ecosystems. Elevated acidity in a lake or river is directly harmful to fish because it corrodes the organic gill material and attacks the calcium carbonate skeleton. In addition, the acidity dissolves toxic metals such as aluminum from the sediments. There is also ample evidence that acid rain is harmful to terrestrial vegetation, mostly because it leaches nutrients such as potassium and allows them to exit the ecosystem by runoff.

See also: Acid Rain.

Acid Gas

Many gas streams, while ostensibly being hydrocarbon in nature, contain large amounts of acid gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) and acid gas is natural as or even process gas that contains significant amounts of hydrogen sulfide, carbon dioxide, or similar contaminants. The terms acid gas and sour gas are often (incorrectly) treated as synonyms.

A gas stream containing hydrogen sulfide or carbon dioxide is referred to as sour and a gas stream that is free from hydrogen sulfide is referred to as *sweet*. The corrosive nature of hydrogen sulfide and carbon dioxide in the presence of water (giving rise to an acidic aqueous solution) and because of the toxicity of hydrogen sulfide and the lack of heating value of carbon dioxide. However, because gas streams from a variety of renewable sources have a wide range of composition, including the concentration of the two acid gases, processes for the removal of acid gases vary and are subject to choice based upon the desired end-product.

In addition to hydrogen sulfide and carbon dioxide, a gas stream may contain other contaminants, such as mercaptan derivatives (such as methyl mercaptan, CH_3SH , and carbonyl sulfide, COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes are also capable of removing the acid gas impurities to low levels when the acid gases are there in low to medium concentrations in the gas.

To sweeten (i.e., remove sulfur compounds from) the high acid content gas, it is first pre-scrubbed to remove entrained brine, hydrocarbons, and other constituents. The sour gas then enters an absorber, where lean amine solution chemically absorbs the acid gas components, as well as a small portion of hydrocarbons, rendering the gas ready for processing and sale. An outlet scrubber removes any residual amine, which is regenerated for recycling. Hydrocarbon contaminants entrained in the amine can be separated in a flash tank and used as fuel gas or sold.

Process efficiency can be optimized by mixing different types of amine to increase absorption capacity, by increasing the amine concentration, or by varying the temperature of the lean amine absorption process.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Acid Gas Removal

Acid gas removal (acid gas treating) is the removal of acidic gases such as hydrogen sulfide and carbon dioxide from gas streams. In addition to removal water and gas stream liquids removal, one of the most important parts of gas processing involves the removal of hydrogen sulfide and carbon dioxide. Gas from some sources contains significant amounts of hydrogen sulfide and carbon dioxide and is usually referred to as sour gas. Sour gas is undesirable because the sulfur compounds it contains can be extremely harmful, even lethal, to breathe and the gas can also be extremely corrosive. The process for removing hydrogen sulfide from sour gas is commonly referred to as sweetening the gas.

Acid gas removal (i.e., removal of carbon dioxide and hydrogen sulfide from gas streams) is achieved by application of one or both of the following process types: (i) absorption and (ii) adsorption.

Acid gas removal processes involve the chemical reaction of the acid gases with a solid oxide (such as iron oxide) or selective absorption of the contaminants into a liquid (such as ethanolamine) that is passed countercurrent to the gas. Then the absorbent is stripped of the gas components (regeneration) and recycled to the absorber. The process design will vary and, in practice, may employ multiple absorption columns and multiple regeneration columns.

Liquid absorption processes (which usually employ temperatures below 50°C (120°F) are classified either as physical solvent processes or chemical solvent processes. The former processes employ an organic solvent, and absorption is enhanced by low temperatures, or high pressure, or both. Regeneration of the solvent is often accomplished readily. In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkaline solutions such as amines or carbonates. Regeneration (desorption) can be achieved by the use of reduced pressure and/or high temperature, whereby the acid gases are stripped from the solvent.

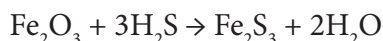
Adsorbers are widely used to increase a low gas concentration prior to incineration unless the gas concentration is high in the inlet air stream. Adsorption also is employed to reduce problem odors from gases. There are several limitations to the use of adsorption systems, but it is generally felt that the major one is the requirement for minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency.

The precise area of application of a given process is difficult to define, and several factors must be considered: (i) the types and concentrations of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

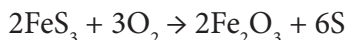
A number of processes are available for the removal of hydrogen sulfide from gas streams. These processes can be categorized as those based on physical absorption, adsorption by a solid, or chemical reaction. Physical absorption processes suffer from the fact that they frequently encounter difficulty in reaching the low concentrations of hydrogen sulfide required in the sweetened gas stream.

Solid bed adsorption processes suffer from the fact that they are generally restricted to low concentrations of hydrogen sulfide in the entering sour gas stream. The development of a short-cycle adsorption unit for hydrogen sulfide removal might help remove part of this low-concentration restriction for the solid bed absorption processes. In general, chemical processes are able to meet the regulated hydrogen sulfide levels.

The most well-known hydrogen sulfide removal process is based on the reaction of hydrogen sulfide with iron oxide (iron sponge process or dry box method) in which the gas is passed through a bed of wood chips impregnated with iron oxide:



The bed is then regenerated by passage of air through the bed:

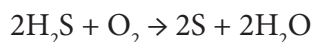
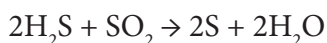
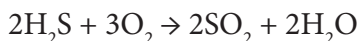


The bed is maintained in a moist state by circulation of water or a solution of soda ash.

The method is suitable only for small-to-moderate quantities of hydrogen sulfide. Approximately 90% of the hydrogen sulfide can be removed per bed but bed clogging by elemental sulfur occurs and the bed must be discarded and the use of several beds in series is not usually economical. Removal of larger amounts of hydrogen sulfide from gas streams requires continuous processes, such as the Ferrox process or the Stretford process.

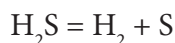
The Ferrox process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid.

Most hydrogen sulfide removal processes involve fairly simple chemistry with the potential for regeneration with return of the hydrogen sulfide. However, if the quantity involved does not justify installation of a sulfur recovery plant, usually a Claus plant, it will be necessary to select a process which produces elemental sulfur directly:



The conversion can be achieved by reacting the hydrogen sulfide gas directly with air in a burner reactor if the gas can be burnt with a stable flame.

Other equilibria which should be taken into account are the formation of sulfur dimer, hexamer, and octamer as well as the dissociation of hydrogen sulfide:



Carbonyl sulfide and carbon disulfide may be formed, especially when the gas is burned with less than the stoichiometric amount of air in the presence of hydrocarbon impurities or large amounts of carbon dioxide.

Equilibrium conversion is almost complete (approximately 99 to 100%) at relatively low temperatures and diminishes at first at higher temperatures, in accordance with the exothermic nature of the reaction. A further rise in temperature causes the equilibrium conversion to increase again. This is a consequence of the dissociation of the polymeric sulfur into monatomic sulfur.

Catalysis by alumina is necessary to obtain good equilibrium conversions: the thermal Claus reaction is fast only above 500°C (930°F). There is also a lower temperature limit which is not caused by low rates but by sulfur condensation in the catalyst pores and consequent deactivation of the catalyst. The lower limit at which satisfactory operation is still possible depends on the pore size and size distribution of the catalyst; with alumina-based catalysts having wide pores, the conversion proceeds satisfactorily at approximately 200°C (390°F).

In all Claus process configurations several conversion steps in adiabatic reactors are used, with intermittent and final condensation of the sulfur produced. There are three main process forms, depending on the concentration of hydrogen sulfide and other sulfur compounds in the gas to be converted, i.e., the straight-through, the split-flow oxidation process.

The straight-through process is applicable when the gas stream contains more than 50% v/v hydrogen sulfide. Feed gases of this type can be burnt with the stoichiometric amount of air to give sulfur. The combustion reactor is followed by a combined waste heat boiler and sulfur condenser from which liquid sulfur and steam are obtained. The gases are then reheated by in-line fuel combustion to the temperature of the first catalytic convertor, which is usually kept at approximately 350°C (660°F) to decompose any carbonyl sulfide and any carbon disulfide formed in the combustion step. A second catalytic convertor, operating at as low a temperature as possible, is also employed to obtain high final conversions.

Molecular sieves and membranes have been undergoing development for the removal of hydrogen sulfide and carbon dioxide from gas streams, especially when the amount of the acid gas(es) is low. The most appropriate use of the sieves and the membranes would be use of the sieve to selectively remove hydrogen sulfide and/or use of membranes permeable to hydrogen sulfide but not to carbon dioxide.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Acid Gas Removal Processes

The primary process for sweetening sour gas streams is similar to the processes of glycol dehydration and removal of gas stream liquids by absorption. In this case, however, amine (olamine) solutions are used to remove the hydrogen sulfide (the amine process). The sour gas is run through a tower, which contains the olamine solution.

There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from the gas stream as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status; the amine solution used can be regenerated for reuse.

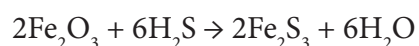
Although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponge to remove hydrogen sulfide and carbon dioxide. Treatment of gas to remove the acid gas constituents (hydrogen sulfide and carbon dioxide) is most often accomplished by contact of the gas stream with an alkaline solution. The most commonly used treating solutions are aqueous solutions of the ethanolamine or alkali carbonates.

A considerable number of other treating agents have been developed in recent years. Most of these newer treating agents rely upon physical absorption and chemical reaction. When only carbon dioxide is to be removed in large quantities or when only partial removal is necessary, a hot carbonate solution or one of the physical solvents is the most economical selection.

The most well-known hydrogen sulfide removal process is based on the reaction of hydrogen sulfide with iron oxide (often also called the iron sponge process or the dry box method) in which the gas is passed through a bed of wood chips impregnated with iron oxide.

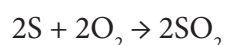
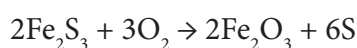
The iron oxide process is the oldest and still the most widely used batch process for sweetening gas streams and separation the gas liquids. The process was implemented during the 19th century. In the process, the sour gas is passed down through the bed. In the case where continuous regeneration is to be utilized a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the on-stream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove.

The process is usually best applied to gases containing low to medium concentrations (300 ppm) of hydrogen sulfide or mercaptans. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is high purity. The use of iron sponge process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:



The reaction requires the presence of slightly alkaline water and a temperature below 43°C (110°F) and bed alkalinity ($\text{pH} = 8$ to 10) should be checked regularly, usually on a daily basis. The pH level is be maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the inlet gas stream.

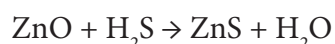
The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:



The regeneration step is exothermic and air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles, this sulfur will form a cake over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles the bed must be removed and a new bed introduced into the vessel.

The iron oxide process is one of several metal oxide-based processes that scavenge hydrogen sulfide and organic sulfur compounds (mercaptans) from gas streams through reactions with the solid based chemical adsorbent. They are typically non-regenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most of the processes are governed by the reaction of a metal oxide with hydrogen sulfide to form the metal sulfide. For regeneration, the metal oxide is reacted with oxygen to produce elemental sulfur and the regenerated metal oxide. In addition, to iron oxide, the primary metal oxide used for dry sorption processes is zinc oxide.

In the zinc oxide process, the zinc oxide media particles are extruded cylinders 3-4 mm in diameter and 4-8 mm in length and react readily with the hydrogen sulfide:



At increased temperatures (205 to 370°C, 400 to 700°F), zinc oxide has a rapid reaction rate, therefore providing a short mass transfer zone, resulting in a short length of unused bed and improved efficiency.

Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stretford process.

The Ferrox process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid. Most hydrogen sulfide removal processes return the hydrogen sulfide unchanged, but if the quantity involved does not justify installation of a sulfur recovery plant (usually a Claus plant), it is necessary to select a process that directly produces elemental sulfur.

The processes using ethanolamine and potassium phosphate are now widely used. The ethanolamine process, known as the Girbotol process, removes acid gases (hydrogen sulfide and carbon dioxide) from liquid hydrocarbons as well as from natural and from refinery gases. The Girbotol process uses an aqueous solution of ethanolamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

The process using potassium phosphate is known as phosphate desulfurization, and it is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbons as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally.

Moisture may be removed from hydrocarbon gases at the same time as hydrogen sulfide is removed. Moisture removal is necessary to prevent harm to anhydrous catalysts and to prevent the formation of hydrocarbon hydrates (such as $\text{C}_3\text{H}_8 \cdot 18\text{H}_2\text{O}$) at low temperatures. A widely used dehydration and desulfurization process is the glycol-amine process, in which the treatment solution is a mixture of ethanolamine and a large amount of glycol. The mixture is circulated through an absorber and a reactivator in the same way as ethanolamine is circulated in the Girbotol process. The glycol absorbs moisture from the hydrocarbon gas passing up the absorber; the ethanolamine absorbs hydrogen sulfide and carbon dioxide. The treated gas leaves the top of the absorber; the spent ethanolamine-glycol mixture enters the reactivator tower, where heat drives off the absorbed acid gases and water.

Other processes include the Alkazid process for removal of hydrogen sulfide and carbon dioxide using concentrated aqueous solutions of amino acids. The hot potassium carbonate process decreases the acid content of natural and refinery gas from as much as 50% to as low as 0.5% and operates in a unit similar to that used for amine treating.

The Giammarco-Vetrocoke process is used for hydrogen sulfide and/or carbon dioxide removal. In the hydrogen sulfide removal section, the reagent consists of sodium or potassium carbonates containing a mixture of arsenite derivatives (such as sodium arsenite, NaAsO_2) and arsenate derivatives (such as sodium arsenate, Na_3AsO_4); the carbon dioxide removal section utilizes hot aqueous alkali carbonate solution activated by arsenic trioxide or selenous acid or tellurous acid.

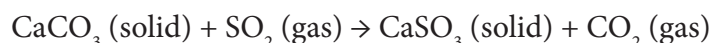
Molecular sieves are highly selective for the removal of hydrogen sulfide (as well as other sulfur compounds) from gas streams and over continuously high absorption efficiency. They are also an effective means of water removal and thus offer a process for the simultaneous dehydration and desulfurization of gas. Gas that has excessively high water content may require upstream dehydration, however.

The molecular sieve process is similar to the iron oxide process. Regeneration of the bed is achieved by passing heated clean gas over the bed. As the temperature of the bed increases, it releases the adsorbed hydrogen sulfide into the regeneration gas stream. The sour effluent regeneration gas is sent to a flare stack, and up to 2% of the gas seated can be lost in the regeneration process. A portion of the gas stream may also be lost by the adsorption of hydrocarbon components by the sieve.

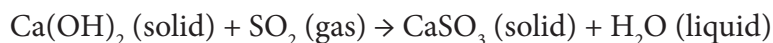
See also: Alkazid Process, Gas Cleaning, Gas Processing, Gas Treating.

Acid Gas Scrubbing – Basic Solid or Solution

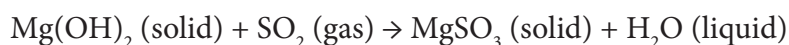
Sulfur dioxide is an acid gas and thus the typical sorbent slurries or other materials used to remove the sulfur dioxide from the flue gases are alkaline. The reaction taking place in wet scrubbing using a limestone (CaCO_3) slurry produces calcium sulfite (CaSO_3):



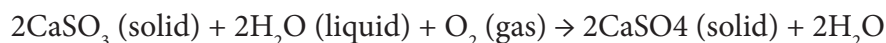
When wet scrubbing with a lime [Ca(OH)_2] slurry, the reaction also produces calcium sulfite:



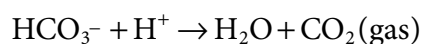
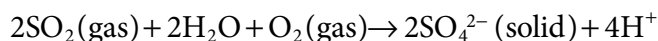
When wet scrubbing with a magnesium hydroxide [Mg(OH)_2] slurry, the reaction produces magnesium sulfite (MgSO_3):



In some designs, the calcium sulfite is oxidized to produce calcium sulfate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$):



Seawater is also used to absorb sulfur dioxide; the SO_2 is absorbed in the water and when oxygen is added reacts to form sulfate ions (SO_4^{2-}) and free protons (H^+) which result in the release of carbon dioxide from the carbonates in the seawater:



See also: Gas Cleaning, Gas Processing, Gas Treating.

Acid Gas Scrubbing – Wet Scrubbers

To promote maximum gas-liquid surface area and residence time, a number of wet scrubber designs have been used in wet flue gas desulfurization systems, including spray towers, venturi scrubbers, plate towers, and mobile packed beds.

Scale buildup, plugging, or erosion affect the dependability and absorber efficiency of flue gas desulfurization systems and the trend has been to use simple scrubbers such as spray towers instead of more complicated ones. The configuration of the tower may be vertical or horizontal, and flue gas can flow co-currently, counter-currently, or cross-currently with respect to the liquid. The chief drawback of spray towers is that they require a higher liquid-to-gas ratio requirement for equivalent sulfur dioxide removal than other absorber designs.

A wet scrubber is a form of pollution control technology and is a device that removes pollutants from gas streams. In a wet scrubber, the polluted gas stream is brought into contact with the scrubbing liquid, by spraying it with the liquid, by forcing it through a pool of liquid, or by some other contact method, so as to remove the pollutants.

Scrubbers can be designed to collect particulate matter and/or gaseous pollutants. Wet scrubbers remove dust particles by capturing them in liquid droplets. Wet scrubbers remove pollutant gases by dissolving or absorbing them into the liquid. Any droplets that are in the scrubber inlet gas must be separated from the outlet gas stream by means of another device referred to as a mist eliminator. Also, the resultant scrubbing liquid must be treated prior to any ultimate discharge or being reused in the plant.

There are numerous configurations of scrubbers and scrubbing systems, all designed to provide good contact between the liquid and polluted gas stream. Examples include a venturi scrubber and the mist eliminator for a venturi scrubber is often a cyclone separator whereas the packed tower design has the mist eliminator built into the top of the tower.

The ability of a wet scrubber to collect small particles is often directly proportional to the power input into the scrubber. Low-energy devices such as spray towers are used to collect particles larger than 5 micrometers. To obtain high efficiency removal of 1 micrometer (or less) particles generally requires high-energy devices such as venturi scrubbers or augmented devices such as condensation scrubbers. Additionally, a meticulously designed and operated entrainment separator or mist eliminator is important to achieve high removal efficiencies. The greater the number of liquid droplets that are not captured by the mist eliminator the higher the potential emission levels.

Wet scrubbers that remove gaseous pollutants are referred to as absorbers. Good gas-to-liquid contact is essential to obtain high removal efficiencies in absorbers. A number of wet scrubber designs are used to remove gaseous pollutants, with the packed tower and the plate tower being the most common.

If the gas stream contains both particle matter and gases, wet scrubbers are generally the only single air pollution control device that can remove both pollutants. Wet scrubbers can achieve high removal efficiencies for either particles or gases and, in some instances, can achieve a high removal efficiency for both pollutants in the same system. However, in many cases, the best operating conditions for particles collection are the poorest for gas removal.

In general, obtaining high simultaneous gas and particulate removal efficiencies requires that one of them be easily collected (i.e., that the gases are very soluble in the liquid or that the particles are large and readily captured) or by the use of a scrubbing reagent such as lime (CaO) or sodium hydroxide (NaOH).

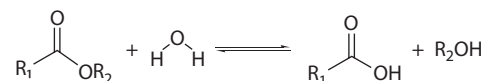
For particulate control, wet scrubbers (also referred to as wet collectors) are evaluated against fabric filters and electrostatic precipitators (ESPs).

Wet scrubbers have the ability to handle high temperatures and moisture and in wet scrubbers, the inlet gases are cooled, resulting in smaller overall size of equipment. Also, wet scrubbers can remove both gases and particulate matter and can neutralize corrosive gases. On the other hand, wet scrubbers are subject to corrosion and there is the need for entrainment separation or mist removal to obtain high efficiencies and the need for treatment or reuse of spent liquid.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Acid Hydrolysis

Hydrolysis is any chemical reaction in which a molecule of water ruptures one or more chemical bonds. The term is used broadly for substitution, elimination, and fragmentation reactions in which water is the nucleophile:



Acid hydrolysis is the means by which cellulosic material can be converted to lower molecular weight products and thence to fuels. Although the chemical transformation steps can be complex, using polysaccharide derivatives (such as starch) The overall process can be represented by a series of simplified steps (Table A-3):

Table A-3 Simplified steps that represent the conversion of polysaccharide derivatives to methane.

Polysaccharides			
(<i>Hydrolytic bacteria*</i>)			
	Fatty acids		
	(<i>Acidogenic bacteria*</i>)		
		Organic acids	
		(<i>Acetogenic bacteria</i>)	
			Methanogenic substances**
			(<i>Methanogens</i>)

*The names that are italicized and in parentheses are the active agents that cause the chemical transformation.

**The methanogenic substances are precursors to methane and carbon dioxide.

Large amounts of inexpensive and renewable lignocellulose waste are generated each year from forestry and agricultural production. These include fruit processing residues, dairy industry wastes, corn and sugar by-products, and paper industry wastes. Lignocellulosic biomass can be converted to biofuels such as ethanol and hydrogen via simple sugars. Lignocellulose is a composite of cellulose fibres embedded in a cross-linked lignin-hemicellulose matrix. It gives structure and strength to plants. Although abundant, lignocellulosic waste is difficult to convert to fermentable sugars because of its complex chemical structure: its three major components (cellulose (crystalline and amorphous) hemicellulose and lignin) must be processed separately (Lee et al., 2007).

Cellulose consists of linear, highly ordered chains of glucose and is one of the most abundant biopolymers on the planet. When produced by plants, it has both highly amorphous regions containing large voids and other irregularities as well as tightly packed crystalline regions. It also accumulates in the environment because it is resistant to most forms of degradation. Hemicellulose is a complex polymer of a variety of sugars. This mix of sugars mainly consists of six-carbon and five-carbon sugars. Lignin is a poly-phenolic polymer that fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components. It is covalently linked to hemicellulose and crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall, and by extension, the plant as a whole. The content of cellulose, hemicellulose and lignin in common agricultural residues depends upon the source and origin of the feedstocks. However, because lignocellulosic biomass is so complex, it is difficult to use as a feedstock for bio-fuel. A variety of physical, chemical, and enzymatic processes have been developed to fractionate lignocellulose into the major plant components of hemicellulose, cellulose, and lignin.

Ethanol is produced from lignocellulose via pre-treatment, hydrolysis, fermentation, and distillation. The goal of pre-treatment is to increase the surface area of lignocellulosic material, making the polysaccharides more susceptible to hydrolysis, by separating the xylose and lignin from the crystalline cellulose. Pre-treatment must also avoid the

degradation or loss of precious carbohydrates and avoid the formation of by-products that can inhibit subsequent steps. However, pre-treatment often produces biological inhibitors, which affect fermentation. A large variety of pre-treatment processes have been developed. Common pre-treatments are steam-explosion, acid treatment, biological methods, and comminution. These methods can be used singly or in combination.

Steam explosion involves saturation of the pores of plant materials with steam followed by rapid decompression. The explosive expansion of steam reduces the plant material to separated fibres, increasing accessibility of polysaccharides to subsequent hydrolysis. Ammonia fibre explosion (AFEX) is similar to steam explosion except that liquid ammonia is used. It is effective on agricultural residues but has not been successful in pre-treating woody biomass. *Biological pre-treatments* employ microorganisms that produce lignin-degrading enzymes (ligninase). *Comminution* is an integral part of pre-treatment and uses a hammer mill to produce particle sizes that can pass through 3 mm screen openings.

The mechanisms by which pre-treatments improve the digestibility of lignocellulose are not well understood. Pre-treatment effectiveness has been correlated with removal of hemicellulose and lignin (lignin solubilisation is beneficial for subsequent hydrolysis but may also produce derivatives that inhibit enzyme activity). Some pre-treatments reduce the crystallinity of cellulose, which improves reactivity, but this does not appear to be the key for many successfully pre-treatments.

Hemicellulose is readily hydrolysed to pentoses (5 carbon sugars) but pentoses are difficult to ferment. The cellulose hydrolyses to hexoses (6 carbon sugars). Crystalline cellulose is difficult to hydrolyse but the resulting hexose derivatives are readily fermented. The three basic methods for hydrolysing structural polysaccharides to fermentable sugars (glucose, xylose, arabinose) are concentrated acid hydrolysis, dilute acid hydrolysis and enzymatic hydrolysis.

Acid treatment is the use of acid to hydrolyze cellulosic materials. Two acid processes hydrolyze both hemicellulose and cellulose with minimal pre-treatment beyond comminution of the lignocellulosic material to particles of approximately 1 mm in size. These are concentrated and dilute acid hydrolysis. *Concentrated acid hydrolysis* dissolves carbohydrates in woody biomass to form a homogeneous gelatine with acid where cellulose is extremely susceptible to hydrolysis. Typically, this is achieved with 70 to 90% v/v sulfuric acid (H_2SO_4) at room temperature, leaving lignin. Before fermentation, the solution of oligosaccharides is diluted to 4% v/v sulfuric acid and (i) heated (at the boiling point) for four hours or (ii) processed using an autoclave at 120°C (248°F) for one hour to yield monosaccharides. Following neutralisation with limestone, the sugar solution is fermented. The procedure takes 10 to 12 hours. Concentrated acid hydrolysis is attractive because it is relatively simple, and high sugar yields (approach 100% of theoretical hexose yields in pure samples and 90% in mixed samples which replicate municipal waste mixtures) are achieved. However, corrosion resistant equipment is necessary and acid recovery is expensive.

Dilute acid hydrolysis (1% acid w/w) greatly reduces the amount of acid required to hydrolyse lignocellulose. The process is accelerated at elevated temperatures: 100 to 160°C (212 to 320°F) for hemicellulose and 180 to 220°C (356 to 428°F) for cellulose. The high temperatures cause oligosaccharides released from the lignocellulose to decompose, greatly reducing yields of simple sugars to only 55 to 60% w/w of the theoretical yield. The decomposition products include toxins (acetic acid, furfural) which inhibit fermentation.

See also: Hydrolysis – Lignocellulosic Materials.

Acidity and Alkalinity

Acidity as applied to natural water and wastewater is the capacity of the water to neutralize hydroxyl ions (OH^-). It is analogous to alkalinity, the capacity to neutralize the hydrogen ion (H^+). Acidity is the quantitative expression of the capacity of the water to neutralize a strong base to a designated pH and an indicator of how corrosive water is.

Acidity can be caused by weak organic acids, such as acetic and tannic acids, and strong mineral acids including sulfuric and hydrochloric acids. However, the most common source of acidity in unpolluted water is carbon dioxide in the form of carbonic acid (H_2CO_3). On the other hand, The alkalinity of water refers to the capability of water to neutralize acid in which the water has a buffering capacity – a buffer is a solution to which an acid can be added without changing the concentration of available hydrogen (H^+) ions (without changing the pH) appreciably.

A surface water body, such as a lake, the alkalinity in the water comes mostly from the rocks and land surrounding the lake. Precipitation falls in the watershed surrounding the lake and most of the water entering the lake comes from runoff over the landscape. If the landscape is in an area containing rocks such as limestone then the runoff picks up

chemicals such as calcium carbonate (CaCO_3), which raises the pH and alkalinity of the water. In areas where the geology contains large amounts of granite, for instance, lakes or ponds may have a lower alkalinity.

The acidity and/or the alkalinity of a surface water system can be influenced by the production of the products of the use of non-renewable fuels, such as those carbonaceous fuels that produce carbon dioxide during use or conversion to other forms of energy. However, switching from non-renewable (fossil fuels) to renewable fuels such as biomass is not always the answer. When biomass is directly used as a fuel or when biomass is used as a process feedstock the products can be sufficiently acidic, and it causes a change in the acidity or alkalinity of surface water systems.

See also: Acid Number.

Acid Number

The acid number (also known as the acidity, the acid value, and the neutralization number) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of the substance. The acid number (AN) or the total acid number (TAN) of crude oil is a measure of the amount of carboxylic acid groups and other acidic species (such as phenols and naphthol derivatives) in crude oil and indicates the potential corrosion during refining.

The acid number is used to quantify the amount of acid present, for example in a sample of biodiesel. It is the quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralize the acidic constituents in 1 g of sample.

$$AN = (V_{eq} - b_{eq})N \frac{56.1}{W_{oil}}$$

In this equation, V_{eq} is the amount of titrant (ml) consumed by the crude oil sample and 1 ml spiking solution at the equivalent point, b_{eq} is the amount of titrant (ml) consumed by 1 ml spiking solution at the equivalent point, and 56.1 is the molecular weight of potassium hydroxide.

The molarity concentration of titrant (N) is calculated as such:

$$N = \frac{1000W_{KHP}}{204.23V_{eq}}$$

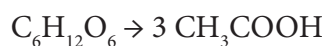
In the equation, W_{KHP} is the amount (g) of KHP in 50 ml of KHP standard solution, V_{eq} is the amount of titrant (ml) consumed by 50 ml KHP standard solution at the equivalent point, and 204.23 is the molecular weight of KHP.

There are standard methods for determining the acid number, such as ASTM D974 and (for mineral oils, biodiesel), or specifically for biodiesel (ASTM D664). The acid number (mg KOH/g oil) for biodiesel should be lower than 0.50 mg KOH/g standard fuels.

See also: Acidity and Alkalinity, Neutralization Number.

Acidogenesis

Acidogenesis (sometimes referred to as fermentation) is the biological process that results in further breakdown of the remaining components by acidogenic (fermentative) bacteria. In this process, volatile fatty acids are produced, along with (depending upon the feedstock) ammonia, carbon dioxide, and hydrogen sulfide, as well as other byproducts. Thus:



Whereas the production of volatile fatty acids (VFAs) is increased when the process pH is in excess of 5, the production of ethanol (C_2H_5OH) is characterized by a pH lower than 5 with reaction process coming to a halt at a pH less than 4.

In a balanced bacterial process approximately 50% of the monomers (glucose, xylose, amino acids) and long-chain fatty acids (LCFA) are broken down to acetic acid (CH_3COOH). Twenty percent is converted to carbon dioxide (CO_2) and hydrogen (H_2), while the remaining 30% is broken down into short-chain volatile fatty acids (VFAs). Fatty acids are monocarboxylic acids that are found in fats and have fewer than six carbon atoms whereas long-chain fatty acids. If there is an imbalance in the digester process, the relative level of volatile fatty acids will increase with the risk of accumulation, since the bacteria that degrade the volatile fatty acids have a slow growth rate and cause an imbalance between the various phases of the process. A steady degradation of the volatile chain fatty acids is therefore crucial and often a limiting factor for the biogas process.

Hydrolysis of simple fats results in 1 mol glycerol and 3 mol long-chain fatty acids and, therefore, high proportions of fat in the digester feedstock will result in large amounts of long-chain fatty acids, while large amounts of protein, which contain nitrogen in amino groups ($-NH_2$), will produce large amounts of ammonium/ammonia (NH_4^+/NH_3). In both cases this can lead to inhibition of the subsequent decomposition phase, particularly if the composition of the biomass feedstock varies.

See also: Acetogenesis, Acidogenesis, Acidogenic Digestate, Anaerobic Digestion, Methanogenesis.

Acidogenic Digestate

Anaerobic digestion produces two main products: (i) digestate and (ii) biogas.

The digestate is the material remaining after the anaerobic digestion of a biodegradable feedstock which is then used as a source of renewable energy through the participation of a variety of chemical reactions (Table A-4).

Acidogenic digestate is fibrous and comprises structural plant material which includes lignin and cellulose. It is the acidogenic digestate that possesses the high moisture retention properties and the raw digestate usually also contains minerals and the remains of the micro-organisms (mainly bacteria) which were active during the digestion process. On the other hand, methanogenic digestate is a liquid or sludge (sometimes referred to as a liquor) which is often high in nutrients such as ammonium derivatives and phosphate derivatives.

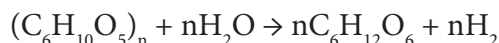
Table A-4 Common reactions in anaerobic digestion process.

Substrate	Reactions
Alcohol derivatives	$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$ $CH_3OH + H_2 \rightarrow CH_4 + H_2O$ $4HCOO^- + 2H^+ \rightarrow CH_4 + 2H_2O$
Monosaccharide derivatives	$C_6H_{12}O_6 + 2H_2O \rightarrow 2H_2 + \text{butyrate} + 2HCO_3^- + 3H^+$ $C_6H_{12}O_6 + 4H_2O \rightarrow 4H_2 + 2CH_3CO_2^- + 2HCO_3^- + 4H^+$
Organic acid derivatives	$C_3H_9CO_2^- + 3H_2O \rightarrow 3H_2 + CH_3CO_2^- + HCO_3^- + H^+$ $C_4H_9CO_2^- + 2H_2O \rightarrow 2H_2 + 2CH_3CO_2^- + H^+$ $HCOO^- + 3H_2 + H^+ \rightarrow CH_4 + 2H_2O$ $CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$ $4CH_3NH_2 + 2H_2O + 4H^+ \rightarrow 3CH_4 + CO_2 + 4NH_4^+$
Methanogenic substances	$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$ $4H_2 + 2HCO_3^- + H^+ \rightarrow \text{acetate} + 4H_2O$
Sulfate derivatives	$4H_2 + SO_4^{2-} \rightarrow HS^- + 3H_2O + OH^-$

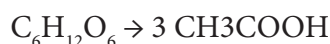
Key: acetate $CH_3CO_2^-$, propionate $C_3H_9CO_2^-$, butyrate $C_4H_9CO_2^-$

There are four stages to the digestion process, each of which has different characteristics: (i) hydrolysis, which is a chemical reaction where particulate matter (solid matter, such as carbohydrate derivatives) is solubilized and high molecular weight chemicals are converted into lower molecular weight products, (ii) acidogenesis, which is a biological reaction in which lower molecular weight products are converted into volatile fatty acid derivatives, (iii) acetogenesis, which is a biological reaction in which the volatile fatty acid derivatives are converted into acetic acid where volatile fatty acids are converted into acetic acid, carbon dioxide, and hydrogen, and (iv) methanogenesis, which is a biological reaction in which acetate derivatives are converted into methane and carbon dioxide, while hydrogen is consumed. Thus, using carbohydrate derivatives as the example of the digester feedstock:

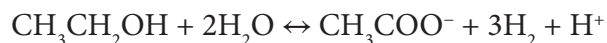
(i) Hydrolysis



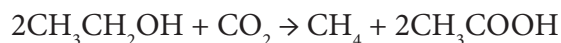
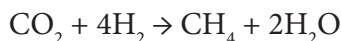
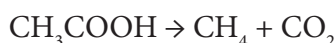
(ii) Acidogenesis



(iii) Acetogenesis



(iv) Methanogenesis



The acidogenic digestate is a stable organic material comprised largely of lignin and chitin, but also of a variety of mineral components in a matrix of dead bacterial cells and some plastic may be present. This resembles domestic compost and can be used as compost or to make low-grade building products such as fiberboard. Another byproduct is a liquid (methanogenic digestate) that is rich in nutrients and can be an excellent fertilizer dependent on the properties of the digester feedstock (Table A-4).

If the feedstock sent to the digester includes low levels of toxic heavy metals (i.e., metals with relatively high density, atomic weight, or atomic number) or synthetic organic chemicals such as pesticides or polychlorobiphenyls, the effect of digestion is to concentrate such materials in the product (i.e., the digester liquor). In such cases further treatment will be required in order to dispose of this liquid properly. In extreme cases, the disposal costs and the environmental risks posed by such materials can offset any environmental gains provided by the use of biogas. This is a significant risk when treating sewage from industrialized catchments.

See also: Anaerobic Digestion, Digester, Digestion.

Acid Rain

Acid rain, or acid deposition, is a broad term that includes any form of precipitation with acidic components, such as sulfuric acid or nitric acid that fall to the ground from the atmosphere in wet or dry forms. This can include rain, snow, fog, hail or even dust that is acidic. Acid rain is another environmental problem that affects much of the eastern United States, damaging crops, forests, wildlife populations, and causing respiratory and other illnesses in humans.

Acid rain is formed when oxides of sulfur and oxides of and nitrogen react with water vapor and other chemicals in the presence of sunlight to form various acidic compounds in the atmosphere. Acid rain results when sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are emitted into the atmosphere and transported by wind and air currents. The sulfur dioxide and nitrogen oxides react with water, oxygen and other chemicals to form sulfuric and nitric acids. These then mix with water and other materials before falling to the ground:



Sulfurous acid



Sulfuric acid



Nitrous acid



Nitric acid



Carbonic acid

These acids can form particulate matter by reaction with, for example, ammonia in the air or with metals particulates.

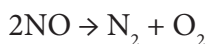
While a portion of the sulfur dioxide and oxides of nitrogen that cause acid rain is from natural sources such as volcanoes, another part is due to the combustion of carbonaceous fuels. Wind currents can carry these oxides over long distances and across borders making acid rain a global problem and not just for those who live close to these sources.

Other pollutants that are emitted as a result of the combustion process are hydrocarbon derivatives (including unburned fuel and hydrocarbon products of the process) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which the nitric oxide is converted to nitrogen dioxide (NO_2) – a brown gas and at sufficiently high levels can contribute to urban haze. However, nitrogen dioxide can absorb sunlight and break apart to produce oxygen atoms that combine with the oxygen in the air to produce ozone (O_3), a powerful oxidizing agent, and a toxic gas.

A final comment related to acid rain since the formation of the rain is usually also attributed to the combustion of fossil fuels and fossil fuel products. Caution is advised when making such a grandiose statement. Any renewable energy source that contains nitrogen and/or sulfur will contribute to the formation of acid rain. In fact, when air is used as the oxidant in a combustor, part of the nitrogen in the air can be converted to nitrogen oxides and thence to acid rain. In all cases, as the fossil fuel users have learned, the gas from combustors such be cleaned and pollutants – such as the oxides of nitrogen and the oxides of sulfur as well as the oxides of carbon – should be removed as soon as possible after they appear from the combustor.

In areas where the biosphere is sensitive to acid rain, there has been ample evidence of the negative effects of acid rain on freshwater ecosystems. Elevated acidity in a lake or river is directly harmful to fish because it corrodes the organic gill material and attacks the calcium carbonate skeleton. In addition, the acidity dissolves metals that (such as aluminum from the sediments) that are toxic to flora and fauna (including humans). There is also evidence that acid rain is harmful to vegetation by a reverse effect insofar as the rain leaches nutrients (such as potassium) from the soil and allows the nutrients to exit the ecosystem by runoff.

Methods of mitigating acid rain formation include (i) reducing the sulfur content of fuels, (ii) using scrubbers such as flue gas desulfurization, (iii) lime injection multi-stage burning, (iv) fluidized bed combustion, or (iv) circulation dry scrubbing of the gas stream. To reduce the formation of nitrogen oxides, methods such as (i) changing air to fuel ratio, (ii) reducing the combustion temperature, which reduces the formation of the oxides of nitrogen that are formed when air is the combustion oxidant, and (iii) a selective catalytic reduction process in which injection of reactive chemicals such as ammonia (NH_3) to react with the nitrogen oxides and convert them into nitrogen and oxygen, represented simply as:



See also: Biogas, Biomass, Waste, Wood.

Acid Rain – Formation

Acid rain is formed when sulfur dioxide (SO_2) and the nitrogen oxides (NO_x) react with water vapor and oxidants in the presence of sunlight to produce various acidic compounds, such as sulfuric acid and nitric acid.



Acid rain has a pH less than 5.0 and predominantly consists of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). As a point of reference, in the absence of anthropogenic pollution sources the average pH of rain is approximately 6.0 (slightly acidic; neutral pH = 7.0). In summary, the sulfur dioxide that is produced during a variety of processes will react with oxygen and water in the atmosphere to yield environmentally detrimental sulfuric acid. Similarly, nitrogen oxides will also react to produce nitric acid.

Precipitation in the form of rain, snow, ice, and fog causes approximately 50% of these atmospheric acids to fall to the ground as *acid rain*, while approximately 50% fall as dry particles (particulate matter, such as soot or aerosol particles) and gases. Winds can blow the particles and compounds hundreds of miles from their source before they are deposited, and they and their sulfate and nitrate derivatives contribute to atmospheric haze prior to eventual deposition as acid rain. The dry particles that land on surfaces are also washed off by rain, increasing the acidity of runoff.

The principle source of acid rain causing pollutants, sulfur dioxide and nitrogen oxides, are coal-fired power plants. Since natural gas emits virtually no sulfur dioxide, and up to 80% less nitrogen oxides than the combustion of coal, increased use of natural gas could provide for fewer acid rain-causing emissions.

Acid Rain – Mitigation

Acid rain reduction can be done either fuel switching or scrubbing. Fuel switching includes limiting the use of Sulphur-containing fuels such as coal or switching to low sulphur-containing coal or oil, switching to alternative energy sources such as using gas boilers instead of coal or oil boilers, nuclear power generation, using renewable energy sources such as wind, air, wave and geothermal energy.

Gas cleaning (gas scrubbing) includes use of electrostatic precipitators where positively charged sulphur particles are attracted by negatively charged plate or chemical means either wet scrubbing such as injecting water or chemical solution such as flue gas desulphurization (FGS) which has the sulfur dioxide removal rate between 80-95% or dry scrubbers such as lime injection multi stage burning (LIMB) or fluidized bed combustion (FBC or circulation dry scrubber) that react with sulphur in the absence of water medium.

To reduce nitrogen oxides (NO_x), methods such as selective catalytic reduction process (SCR) which has the NO_x reduction rate up to 80% where injection of reactive chemicals such as ammonia reacts with NO_x and convert into nitrogen and oxygen, changing air to fuel ratio and changing the combustion temperature. In automobile NO_x reduction, catalytic converters are used, e.g., three-way catalytic converters: (i) conversion of nitrogen oxides into nitrogen and oxygen, (ii) conversion of carbon monoxide into carbon dioxide, and (iii) conversion of hydrocarbon derivatives into carbon dioxide and water.

See also: Acid Rain, Gas Cleaning, Gas Processing, Gas Treating.

Acid Treating

Acid treating is one of the older treating processes in refining of liquids from renewable sources. This process found importance in the earlier days of crude oil refining and was preferentially used by oil industry for treating middle distillates like gasoline, kerosene, etc., and also for the refining of lubricating oils. Used oil refining was also carried out using this process. Primarily, acid treating processes were used to improve color, odor, removal/reduction of aromatic content and other undesirable constituents such as polar nitrogen containing compounds and/or some of the trace metals present in the products. Removal of these undesired constituents leads to considerable improvement in physical properties of the treated petroleum / petrochemical product.

Sulfuric acid treating is known to be one of the oldest and best suited treating agent for a large variety of petroleum-related applications. Use of sulfuric acid was widely accepted as an acid treating agent for upgrading petroleum products. Although petroleum refining industry and researchers have used other acids like hydrofluoric acid, hypochlorous acid for treating of the petroleum products, such as lubricating oil, best performance and economics of the operation could be achieved by using sulfuric acid treating only.

In the process, a product is thoroughly mixed with the acid in a mixer and this mixture is allowed to settle for some time for achieving complete phase separation of aqueous and organic layers. Treated product, i.e., upper organic layer is removed and water washed to give the finished product. If still better quality product is desired with further improvement in color and/or removal of polar constituents, this acid treated product layer may be further treated with clay then followed by water washing as per the process requirements. The bottom layer, i.e., acidic

aqueous layer is taken out from the bottom of the settling tank for the recovery of extracted petroleum products and the recycle of the acid for further product treating or dilute acid; if it cannot be used further then this acid is treated with alkali to neutralize it and it is sent to disposal to water treatment plant.

As in the other treating processes in crude oil refining, acid treatment may also be used as a simple single-stage extraction process, or if required, as a complex multi-stage extraction process. The process requirements and treating scheme is designed based on the nature of the product to be treated and extent of product quality improvement requirement.

Pre-treating and post-treating of the products before and after acid treating also plays a significant role in product quality enhancement by acid treating. Whether it should be clay treatment or simple water washing after acid treating, the overall process requirement can be optimized easily depending upon quality requirements of the finished product. As discussed earlier, clay treatment after acid treating further reduces the polar constituents present in the product besides improving the color of the product. If desired product quality is achieved by acid treatment only then clay treatment step is not essential and simple water washing can give the desired product quality.

A number of process-related parameters play significant roles for the optimization of process requirements and these parameters depend upon the extent of refining needed. Acid concentration is the primary and most important of such requirements; generally lower acid concentrations, around 25% or less are used for the treatment of the alkaline sludge generated in various refinery processes, by neutralizing it before its safe disposal to the water treatment plant. Moderate to strong acid requirement are effectively used in polymerization of olefins and diolefins.

Treatment of higher viscosity products require strong acid concentrations. With varying acid concentrations ease of separation of the acid and organic layer can also be achieved. With dilute acids the phase separation is easy as compared to the strong acids. Fuming sulfuric acid is also used for the treatment of the lube oils and the petroleum products. Another process parameter is operating or treating temperature. Temperature also plays a significant role in quality of treatment and subsequently the end product. Other parameters like contact time, numbers of stages, etc., are equally important in the treatment of products.

Disposal of acidic sludge or waste is a serious problem for the refineries. Safe handling of acidic sludge and its disposal is not at all an easy process. Therefore, refineries have avoided acid handling. Older refineries also, which were earlier using acid treating, have also shifted to environmentally safe and less hazardous treating technologies for improving product quality.

See also: Refining.

Acid Value

The acid value (sometimes referred to as the neutralization number, the acid number, or the acidity) is the amount of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of a chemical substance. It is a measure of the number of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds.

In a typical procedure, a known amount of sample dissolved in an organic solvent (often an alcohol, such as isopropanol) and titrated with a solution of potassium hydroxide (KOH) of known concentration using an indicator (such as phenolphthalein) to monitor the color change and thereby determine the neutralization point as a colour indicator (see ASTM D664. Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration).

As an example, the acid number is used to quantify the acidity of a substance such as biodiesel. As oil-fats become rancid, the triglyceride derivatives are converted into fatty acid derivatives and glycerol, thereby causing an increase in acid number. A similar observation is that of biodiesel aging through analogous oxidation processes and when subjected to prolonged high temperatures (ester thermolysis) or through exposure to acids or bases (acid/base ester hydrolysis).

See also: Acidity and Alkalinity, Acid Number, Neutralization Number.

Activated Sludge Process

Activated sludge consists of sludge particles, teeming with living organisms, produced in either raw or settled wastewater by the growth of organisms (which include bacteria) in aeration tanks where dissolved oxygen is present.

In general, sludge is defined on the basis of the solids content (Figure A-1) but in order to develop a quantitative definition of sludge which will also help with correlating waste forms with disposal options, a simple and measurable characteristic of all three waste forms needs to be identified.

<i>Waste form</i>	<i>Solid,</i>	<i>Sludge</i>	<i>Liquid</i>
<i>Total solids, % w/w</i>	50 to 100	1 to 50	<1%

Figure A-1 Simplified distinction between solid waste, sludge, and liquid waste.

Activated sludge processes treat waste streams that contain 1% or less of suspended solids. In this process, flocculated biological growths are continuously circulated in contact with organic wastewater in the presence of oxygen. The process is widely used for industrial wastes and is even more common in municipal treatment plants.

In the process, air or pure oxygen is bubbled through industrial wastewater combined with organisms to develop a biological floc, which reduces the organic content of the wastewater.

The combination of industrial wastewater and biological mass is commonly known as mixed liquor. Once the industrial wastewater has received sufficient treatment, excess mixed liquor is discharged into settling tanks and the treated supernatant liquid is run off to undergo further treatment before discharge. Part of the settled material (sludge) is returned to the head of the aeration system to re-seed the new sewage (or industrial wastewater) entering the tank. Excess sludge which eventually accumulates beyond what is returned is the waste activated sludge which is removed from the treatment process to keep the ratio of biomass to food supplied (wastewater) in balance. The waste activated sludge is stored away from the main treatment process in storage tanks and is further treated by digestion, either under anaerobic or aerobic conditions prior to disposal.

See also: Chemical Waste, Sludge.

Additives – Catalysts in Combustion Systems

Additives may catalyze or otherwise affect combustion processes. For example, salt has long been known to be of some assistance in removing soot deposits from chimneys and the carbonaceous feedstock treated with a more complex mixture of metal oxides has been reported to be activated in combustion systems but it is apparently not resolved whether the catalytic effect is with regard to carbon-oxygen reactions or whether it is more indirect since the effect resembles (to a degree) the catalysis of feedstock-steam systems in which alkali salts serve to catalyze the carbon-steam reaction to produce synthesis gas (carbon monoxide/hydrogen mixtures). This mixture may then, in turn, react to produce hydrocarbons and oxygenated materials in the presence of the multitude of trace metals that can (and do) occur in biomass feedstocks.

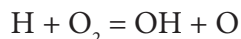
In addition to causing objectionable stack emissions, ash and volatile inorganic material generated by thermal alteration of mineral matter in the feedstock will adversely affect heat transfer processes by fouling heat-absorbing and radiating surfaces and will also influence the performance of the combustion system by causing corrosion, and operating procedures must therefore provide for effective countering of all these hazards.

Corrosion is mainly caused by oxides of sulfur, but in certain parts of a combustion system, specifically on furnace wall tubes with metal temperature of 290 to 425°C (550 to 800°F) and superheater or reheater tubes with temperatures in the range 600 to 700°C (1,110 to 1,300°F), corrosion can be induced by tube deposits that destroy protective surface oxide coatings.

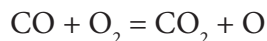
Corrosion damage that is usually ascribed to sulfur is actually caused by sulfuric acid, which is generated from organic and inorganic sulfur-bearing compounds:



Oxidation of sulfur dioxide to sulfur trioxide occurs mostly in flames where (transient) atomic oxygen species are thought to be prevalent by interactions of hydrogen atoms with oxygen:



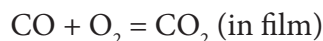
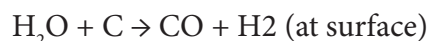
As well as by interactions of carbon monoxide with oxygen:



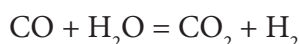
The process can be catalyzed by the ferric oxides which form on boiler tube surfaces and show excellent catalytic activity for sulfur dioxide oxidation at approximately 600°C (1110°F), i.e., at temperatures which occur in the super-heater section of a boiler.

The presence of water has a marked effect on combustion (by participating in various combustion reactions) and there is evidence for the existence of active centers for chain reactions involved in the further combustion of carbon monoxide and hydrogen (which would be reaction intermediates in the combustion process).

The endothermic steam-carbon reaction is primarily responsible for cooling effects in furnaces and the presence of moisture is believed to cause heat generation at the surface of the bed and in the combustion by virtue of the (endothermic) formation of carbon monoxide and hydrogen in the bed which then burn at the surface. On the other hand, the presence of water vapor appears to assist in the formation of carbon dioxide:

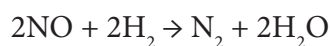
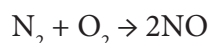
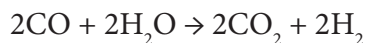


Moisture appears to play a more integral role in the combustion of hydrogen-deficient carbonaceous fuels (such as coal) than has been generally recognized. The carbon-steam reaction to produce carbon monoxide and hydrogen (which are then oxidized to the final products) is an important stage in the combustion sequence as is the carbon monoxide shift reaction to yield carbon dioxide and hydrogen:



Since the whole system involves reaction (and equilibria) between the fuel (i.e., carbon), water, carbon monoxide, hydrogen, and carbon dioxide, the rapid rates of the reactions render it difficult (if not impossible) to determine precisely which of the reactions are the major rate-controlling reactions. In addition, the heterogeneous nature of the system adds a further complication.

The presence of inert gases would usually be expected to dilute the reactants and therefore diminish the reaction rates, such inert materials may actually, on occasion, accelerate the reaction(s). Indeed, the addition of nitrogen to the reaction mixture can be as effective as the addition of oxygen. The nitric oxide formed in the mixture is believed to act as a catalyst:



See also: Combustion.

Additives – Fuels

The term fuel additives applies to chemicals that are intended to improve the capabilities of a gasoline-fuel or diesel-fueled engine while it is running or in use. Fuel stabilizers are designed to keep the fuel in a functional condition when being stored for a long period of time without use. Chemicals may also be added to liquid fuels such as heavy oil and crude shale oil to improve the transportation properties. Pour point depressants have been successful in some instances but are disadvantageous because they only change the physical characteristics of the oil and not its chemical properties.

In modern fuels, a combination of several chemical additives is used in order for the fuel to meet the desired performance level. For example, the use of antiknock additives permits greater efficiency and higher power output because of the higher compression ratios they produce. In certain diesel engines, the higher cetane fuels have shorter ignition delay periods than lower cetane fuels. Several different additives have been tried to increase the cetane number of diesel fuel and lubricity improvers as well as friction modifiers both work through the action of film formation on the metal surfaces. However, biodiesel is, to a point, capable of self-lubricating, thereby reducing friction in diesel engines.

See also: Fuels.

Add-On Environmental Control Methods

There are four general processes used for emission control: (i) adsorption, (ii) absorption, (iii) catalytic oxidation, and (iv) thermal oxidation.

Adsorption is a physico-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid. Subsequently, the captured gas can be desorbed with hot air or steam either for recovery or for thermal destruction. Usually, activated carbon is the adsorbing medium, which can be regenerated upon desorption. Adsorbers are widely used to concentrate a low gas concentration prior to incineration unless the gas concentration is high in the inlet airstream. Adsorption also is employed to reduce odors from gases which have potential odor problems. The only major limitation for an adsorption system is the requirement for minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency.

Absorption differs from adsorption in that it is not a physico-chemical surface phenomenon, but an approach in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (chemisorption). Common absorbing media used are water, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, gas-liquid contactor designs which are employed are plate columns or packed beds.

Catalytic oxidation is used predominantly for destruction of volatile organic compounds (VOCs) and carbon monoxide, these systems operate in temperature regime of 205 to 595°C (400 to 1100°F) in the presence of a catalyst. Without the catalyst the system would require much higher temperatures to operate. Typically, the catalysts used are a combination of noble metals deposited on a ceramic base in a variety of configurations (e.g., honey-comb-shaped) to enhance good surface contact. Catalytic systems are usually classified based on bed types such as fixed-bed (or packed-bed) and fluid-bed. These systems generally have high destruction efficiencies for most volatile organic compounds, resulting in the formation of carbon dioxide, water, and varying amounts of hydrogen chloride (from halogenated hydrocarbons).

Thermal oxidation systems without the use of catalysts, operate at temperatures in excess of 815°C (1,500°F). These operating temperatures are 220-610°C (395-1100°F) higher than catalytic systems.

Particulate matter control (often referred to as dust control) has been one of the primary concerns of industries, since the emission of particulate matter is readily observed through the deposition of fly ash and soot as well as in impairment of visibility. Differing ranges of control can be achieved by use of various types of equipment. Upon proper characterization of the particulate matter emitted by a specific process, the appropriate piece of equipment can be selected, sized, installed, and performance tested. The general classes of particulate matter control devices are: (i) cyclones: wet, dry, axial flow, multi-cyclones, (ii) fabric filters, (iii) wet scrubbers, and (iv) electrostatic precipitators.

Other than settling chambers for large particles, cyclone-type collectors are the most common of the inertial collector class. The particle-laden gas stream enters an upper cylindrical section tangentially and proceeds downward through a conical section. Particles migrate by centrifugal force to the wall and are removed through a seal at the apex of the inverted cone. A reverse-direction vortex moves upward through the cyclone and discharges through a top center opening. Cyclones are often used as primary collectors because of their relatively low efficiency (50-90% is usual). Some small-diameter high-efficiency cyclones are utilized. Particulate matter is removed by centrifugal forces generated by providing a path for the carrier gas to be subjected to a vortex-like spin. Cyclones are effective in removing coarser fractions of particulate matter. The equipment can be arranged in either parallel or series to both increase efficiency and decrease pressure drop.

Fabric filters are typically designed with non-disposable filter bags. As the dusty emissions flow through the filter media (typically cotton, polypropylene, Teflon, or fiberglass), particulate matter is collected on the bag surface as a dust cake. Fabric filters are generally classified based on the filter bag cleaning mechanism employed and operate with collection efficiencies above 99%.

Wet scrubbers are devices in which a counter-current spray liquid is used to remove particles from an airstream. Device configurations include plate scrubbers, packed beds, orifice scrubbers, venturi scrubbers, and spray towers, individually or in various combinations. Wet scrubbers can achieve high collection efficiencies at the expense of prohibitive pressure drops. These units for particulates operate by contacting the particles in the gas stream with a liquid. In principle, the particles are incorporated in a liquid bath or in liquid particles which are much larger and therefore more easily collected. Other techniques include high-energy input venturi scrubbers, electrostatic scrubbers where particles or water droplets are charged, and flux force/condensation scrubbers where a hot humid gas is contacted with sub-cooled liquid or where steam is injected into saturated gas. In the latter scrubber, the movement of water vapor toward the cold water surface carries the particles with it (diffusiophoresis), while the condensation of water vapor on the particles causes the particle size to increase, thus facilitating collection of fine particles. The foam scrubber is a modification of a wet scrubber in which the particle-laden gas is passed through a foam generator where the gas and particles are enclosed by small bubbles of foam.

Electrostatic precipitators operate on the principle of imparting an electric charge to particles in the incoming airstream, which are then collected on an oppositely charged plate across a high voltage field. The dust cake is then collected from the plate by striking it with rappers. The dust collection efficiency is a strong function of dust resistivity. In general, particles in a gas stream are charged by a high-voltage discharge electrode and collected at collection plates of opposite polarity. Particles of high resistivity create the most difficulty in collection. Because resistivity varies with temperature, this can be an important parameter. Conditioning agents such as sulfur trioxide have been used to lower resistivity. Other important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include high-voltage pulse energization to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of high efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations.

See also: Gas Cleaning, Gas Processing, Gas Treating, Pollution Control.

Adip Process

The Adip process is regenerative amine process for the removal of hydrogen sulfide and carbon dioxide from natural gas, refinery gas, and synthesis gas. The process uses aqueous solutions of the secondary amine, diisopropanolamine, or the tertiary amine, methyl di-ethanolamine. Amine concentrations up to 50% w/w can be applied. Hydrogen sulfide can be reduced to low sulfur levels. The process can also be applied to remove hydrogen sulfide, carbon dioxide, and carbonyl sulfide (COS) from liquefied petroleum gas or natural gas liquid to low levels.

The Adip-X process is a regenerative amine process that is highly suitable for bulk and deep removal of carbon dioxide from gas streams. The process uses aqueous solutions of the tertiary amine, methyl diethanolamine, and an additive.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Adsorption

Adsorption (sometimes referred to as physisorption) is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (*adsorbate*). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption is the process by which the gas is concentrated on the surface of a solid or liquid to remove impurities; carbon is a common adsorbing medium which can be regenerated upon desorption. The term sorption encompasses both processes, while desorption is the reverse process.

Adsorption differs from absorption in that the adsorption process is not a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. Usually, carbon is the adsorbing medium, which can be regenerated upon desorption. The quantity of material adsorbed is proportional to the surface area of the solid, and, consequently, adsorbents are usually granular solids with a large surface area per unit mass. Subsequently, the captured gas can be desorbed with hot air or steam, either for recovery or for thermal destruction.

The number of steps and the type of process used to produce specification-quality gas and liquids most often depend upon the source and makeup of the wellhead production stream. In some cases, several of the steps may be integrated into one unit or operation, performed in a different order or at alternative locations, or not required at all.

If the attractive forces are chemical in nature and result in the formation of a chemical bond between the solid adsorbent and the adsorbed molecules, the adsorption is called chemical adsorption or chemisorption. In the latter case, the removal of the chemisorbed material to regenerate the adsorbent is more difficult and may require chemical techniques to reactivate the spent adsorbent. For this reason, most adsorbents are operated as physical adsorbents with regeneration by reducing pressure, raising temperature, or flushing with solvents. However, even physical adsorbents are often slowly deactivated over many adsorption regeneration cycles by chemisorption due to unknown trace contaminants in either the adsorbent or the feed stream. At some specific deactivation level, the adsorbent must be either reactivated or discarded.

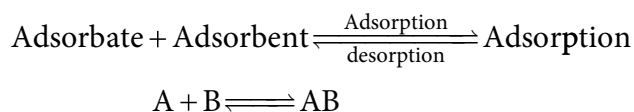
Two general types of adsorbents are commonly used. The first, of which activated carbon is an example, has a low-energy surface and is selective for non-polar molecules. These can be hydrocarbons and other organic compounds of low polarity such as ether derivatives, ketone derivatives, ester derivatives, and halogenated hydrocarbon derivatives. This type of adsorbent is useful for recovery of organic materials from wastewaters and exhaust gases. The other type of adsorbent, which consists of activated clay minerals, alumina minerals, and silica gel, has a higher energy surface that is more selective for polar molecules.

These materials are usually not effective for water solutions because the water selectively covers all the adsorption sites to the exclusion of everything else. However, they do find use for removing polar impurities such as water, oxidation products, or naturally occurring impurities like sulfur and nitrogen compounds from organic process streams. They are also useful for cleaning slightly contaminated waste streams to permit recycling of the major components. Zeolites and molecular sieves are special cases which depend on pore size and structure, i.e., access to the internal surface, for their selectivity rather than on adsorbent surface energy. They can be made from specially treated carbons as well as from natural or synthetic crystalline materials.

See also: Absorption, Adsorption, Adsorption Process, Chemisorption, Gas Cleaning, Gas Processing, Gas Treating, Physisorption.

Adsorption Isotherm

The adsorption process is studied through the development of an *adsorption isotherm* which relates the amount of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been developed by Freundlich, Langmuir, and by means of the Brunauer, Emmett, and Teller (BET) theory. Simply, the adsorption process can be represented as:



Freundlich Adsorption Isotherm

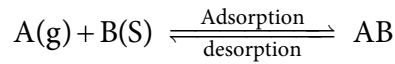
Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure:

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

In this equation, x is the mass of the gas adsorbed on mass, m , of the adsorbent at pressure p ; k and n are constants whose values depend upon adsorbent and gas at particular temperature. This isotherm establishes the relationship of adsorption with lower pressures but is not always suitable for high-pressure situations.

Langmuir Adsorption Isotherm

The *Langmuir adsorption isotherm* is based on several assumptions, one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules:



In this equation, $A(g)$ is the unadsorbed gaseous molecule, $B(s)$ is unoccupied metal surface, and AB is adsorbed gaseous molecule from which a relationship between the number of active sites of the surface undergoing adsorption and pressure can be derived:

$$\theta = \frac{KP}{1 + KP}$$

Here, θ is the number of sites of the surface which are covered with gaseous molecule, P is the pressure, and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase. However, the Langmuir adsorption equation is that it is valid at low pressure only. At lower pressure, KP is small and the factor $1 + KP$ in denominator is close to unity which reduces the Langmuir equation to:

$$\theta = KP$$

At high pressure, KP is large and the factor $1 + KP$ is almost equal to KP , thereby reducing the Langmuir equation to:

$$\theta = \frac{KP}{KP} = 1$$

BET Adsorption Isotherm

The BET theory equation invokes the concept that under the condition of high pressure and low temperature, the thermal energy of gaseous molecules decreases and more and more gaseous molecules would be available per unit surface area. As a result, multilayer adsorption will occur and can be represented by the BET equation:

$$V_{total} = \frac{V_{mono} C \left(\frac{P}{P_0} \right)}{\left(1 - \frac{P}{P_0} \right) \left(1 + C \left(\frac{P}{P_0} \right) - \frac{P}{P_0} \right)}$$

Another form of the BET equation is:

$$\frac{P}{V_{total}(P - P_0)} = \frac{1}{V_{mono}C} + \frac{c-1}{V_{mono}C} \left(\frac{P}{P_0} \right)$$

In these equations, V_{mono} is the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules. Thus:

$$C = K_1/K_L$$

$$\frac{K_1}{K_L}$$

K_1 is the equilibrium constant when a single molecule is adsorbed per vacant site and K_L is the equilibrium constant to the saturated vapor liquid equilibrium.

See also: Adsorption, Adsorption Process.

Adsorption Process

Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. Typically, carbon is the adsorbing medium, which can be regenerated upon desorption, and the quantity of material adsorbed is proportional to the surface area of the solid. Consequently, adsorbents are usually granular solids with a large surface area per unit mass. Subsequently, the captured gas can be desorbed with hot air or steam, either for recovery or for thermal destruction.

Adsorbers are widely used to increase a low gas concentration prior to incineration unless the gas concentration is high in the inlet air stream. Adsorption is also employed to reduce problem odors from gases. There are several limitations to the use of adsorption systems, but it is generally felt that the major one is the requirement for minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency. Absorption differs from adsorption, in that it is not a physical-chemical surface phenomenon, but an approach in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (chemisorption). Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, the gas-liquid contactor designs that are employed are plate columns or packed beds.

Separation by adsorption chromatography essentially commences with the preparation of a porous bed of finely divided solid, the adsorbent. The adsorbent is usually contained in an open tube (column chromatography). The sample is introduced at one end of the adsorbent bed and induced to flow through the bed by means of a suitable solvent. As the sample moves through the bed, the various components are held (adsorbed) to a greater or lesser extent depending on the chemical nature of the component. Thus, those molecules that are strongly adsorbed spend considerable time on the adsorbent surface rather than in the moving (solvent) phase, but components that are slightly adsorbed move through the bed comparatively rapidly.

Numerous factors randomly affect the process of migration through a bed, and in fact, the total distance traveled in a given time by different molecules of the same material is not constant. Nevertheless, the suitable choice of a bed and a moving (solvent) phase allows adequate separation of even multi-component mixtures to be achieved.

Adsorption processes for water treatment are used to remove dissolved metals, organic compounds, and many toxic substances. Carbon which has been *activated* (oxidized at high temperatures) to create millions of minute cavities is an effective and economical means of adsorbing dissolved organic and other chemicals that cannot be removed by filtration.

Granular activated carbon and activated carbon black are used in combination with filtration and/or disinfection to remove undesirable tastes and odors, chloramines, some pesticides and herbicides, and other chemical contaminants. They are sometimes also combined with halogen-based disinfection technologies to remove residual iodine and chlorine. Activated carbon does not remove salts.

Adsorption with regenerated carbon slurries and with resin particles is common, and some systems use activated carbon particles that are contained in a fixed bed, either without regeneration or with regeneration within the column. In all cases, the separation involves physical adsorption of the contaminants on the surfaces of the particulate medium.

See also: Adsorption, Adsorption Isotherm, Gas Cleaning, Gas Processing, Gas Treating.

Advanced Cycloning

Advanced cycloning processes involve the separation of two species of different densities using a medium of an intermediate density to the two species. In the process, the heavy mineral matter component of the coal is separated from its lighter organic matter counterpart. Advanced cycloning technology seeks to extend the density-based separating principle to fine and ultrafine coal through the use of alternative media, such as heavy liquids and micronized magnetic, and through the application of centrifugal force to accelerate the separation process.

The dense medium is generally a suspension of fine, high-density particles (magnetite or sand) with the density of the medium varying directly with the solids concentration. The separating performance and downstream recovery of the dense medium suspension require that the difference in size between dense medium particles (magnetite) and coal particles be significant.

See also: Cyclone Separation, Gas Cleaning, Gas Processing, Gas Treating.

Advanced Flue Gas Desulfurization

Flue gas desulfurization (FGD) is the technology used for removing sulfur dioxide (SO_2) from the exhaust flue gases in power plants that burn coal to produce steam for the steam turbines which, in turn, drive the electricity generators. Sulfur dioxide is responsible for acid rain formation. Tall flue gas stacks disperse the emissions by diluting the pollutants in ambient air and transporting them to other regions. However, such practices do not always remove the pollutants.

Advanced flue-gas desulfurization processes remove acid gas from combustion systems burning coal without expensive scrubbers. Emissions are piped into an absorber, where the acid gases react with an absorbing solution (such as a mixture of lime, water, and oxygen). In the process, the gas is usually passed through a particulate removal unit (such as an electrostatic precipitator) after which the flue gas is increased in pressure and then cooled from approximately 130°C (265°F) to 80°C (175°F). It enters the lowest part of the absorber and is further cooled by water used to wash the inlet duct to prevent a buildup of solids.

The main sulfur dioxide absorption process occurs as the gas is scrubbed by a recirculating limestone slurry. This is taken from the bottom of the absorber and is sprayed downwards from nozzles arranged at five separate levels in the absorber tower. As a result of the process chemistry, the recirculating slurry becomes predominantly gypsum (CaSO_4) and a portion is continuously pumped away for gypsum separation and the removal of water using a hydrocyclone system. A wastewater treatment plant ensures that any water from the flue gas desulfurization process returned to the environment meets quality standards set by the regulatory authority.

See also: Flue Gas, Gas Cleaning, Gas Processing, Gas Treating.

Aerobic Digestion

Aerobic digestion is a bacterial process occurring in the presence of oxygen. Under aerobic conditions, bacteria rapidly consume organic matter and convert it into carbon dioxide. Once there is a lack of organic matter, bacteria die

and are used as food by other bacteria. This stage of the process is known as *endogenous respiration*. Solids reduction occurs in this phase.

Composting is also an aerobic process that involves mixing the wastewater solids with sources of carbon such as sawdust, straw, or wood chips. In the presence of oxygen, bacteria digest both the wastewater solids and the added carbon source and, in doing so, produce a large amount of heat.

In an aerobic system, such as composting, the microorganisms access free, gaseous oxygen directly from the surrounding atmosphere. The end products of an aerobic process are primarily carbon dioxide and water which are the stable, oxidized forms of carbon and hydrogen. If the biodegradable starting material contains nitrogen, phosphorus, and sulfur, the end products may also include their oxidized forms: nitrate (NO_3^-), phosphate (PO_4^{2-}), and sulfate (SO_4^{2-}). In an aerobic system, the majority of the energy in the starting material is released as heat by their oxidation into carbon dioxide and water.

Composting systems typically include organisms such as fungi that are able to break down lignin and cellulose to a greater extent than anaerobic bacteria. It is possible, following anaerobic digestion, to compost the anaerobic digestate, allowing further volume reduction and stabilization. When considering an overall system energy and carbon balance, anaerobic digestion performs better than the main alternative, composting.

The aerobic digestion process was initially used in designs for new plants that normally treated waste activated sludge from treatment systems that did not contain a primary settling process; only waste activated or trickling filter sludge, or mixtures of waste activated or trickling filter sludge. Typically, if a primary settling process was incorporated to the design, anaerobic digestion was the process of choice because reliable techniques to thicken and aerobically digest higher than 4% solids were not established at the time.

Because of tighter effluent standards for both nitrogen and phosphorus being enforced in the United States in the late 1990s, primary clarifiers have slowly been eliminated from the process train to preserve a good carbon-to-nitrogen ratio typically required to achieve successful biological nitrogen removal.

As a result of the combination of the new effluent limits and new techniques that provided the capabilities to control aerobic digestion processes and accurately predict the performance of the system, aerobic digestion has become attractive once again. A number of anaerobic digesters have been converted to aerobic digesters because of their relatively easy operation, lower equipment cost, and because they can produce a better quality supernatant with lower nitrates and phosphorus, therefore, protecting the liquid side upstream. An additional benefit of aerobic digestion is the fact that they can achieve comparable volatile solids reduction with shorter retention periods, they have less hazardous cleaning and repairing tasks, and, typically, do not produce an explosive digester gas.

Anaerobic digestion of animal waste is the primary cause of odors, solids buildup and many diseases in swine, dairy and poultry facilities, processing plants, municipal waste systems, and septic systems. Animal waste concentrated in pits under slatted floors or collected in holding tanks or lagoons has the natural tendency to “go anaerobic.” Anaerobic digestion occurs when the anaerobic microbes are dominant over the aerobic microbes. Anaerobic microbes will naturally become dominant in pits or lagoons because of the lack of oxygen in solutions containing heavy concentrations of animal waste, which results in a high biological oxygen demand (BOD). These microbes feed on the animal waste at the bottom of the pits and lagoons. As they digest waste, large amounts of toxic gases are released due to the digestion processes common to the anaerobic microbes.

The anaerobic digestion of animal waste can be changed to aerobic digestion by proper applications of beneficial aerobic microbes in a highly concentrated form. If aerobic microbes are introduced into an environment that is lacking oxygen, they will begin to build oxygen into this environment as long as they survive and reproduce. Aerobes have the ability to do this in a liquid media or in the soil as long as there is an adequate moisture and food source for them to feed on and reproduce.

Once the aerobic microbes become dominant, the aerobic digestion of waste begins. Aerobic digestion, unlike anaerobic digestion, does not produce the pungent gases. The aerobic process results in a more complete digestion of waste solids, reducing the buildup in pits and lagoons by more than 50% in most cases. The aerobic process also improves the environment of the workers and the animals and helps to keep pathogens in check. With proper application, the anaerobic process is converted to aerobic and overall production cost will be reduced.

See also: Anaerobic Digestion, Digester, Digestion.

Aerosols

An aerosol is a suspension of tiny particles or droplets in the air, such as dust, mist, or fumes. These particles may be inhaled or absorbed by the skin, and can sometimes cause adverse health effects for humans. The aerosol particles can be from natural sources or from anthropogenic sources such as the use of various (gaseous, liquid, or solid) fuels, whether the fuels are from fossil fuel sources or from renewable energy sources such as biomass or waste. Aerosol particles – from whatever the source – play an important role in the climate system because of their direct interaction (absorption and scattering) with solar and terrestrial radiation, as well as through their influence on cloud processes and thereby, indirectly, on radiative fluxes.

The particle size of an aerosol is often determined by the process that generated the particle. Combustion particles usually start out in the range 0.01 to 0.05 micron but combine with each other (agglomerate) to form larger particles. Powder is broken down into smaller particles and released into the air; it is difficult to break down such particles smaller than 0.5 micron. Biological particles usually become airborne from liquid or powder forms, so these particles are usually larger than 0.5 micron.

Aerosol emissions (often collectively classed as particulate matter) from stationary combustion sources burning renewable fuels such as biomass, and waste are a significant source of primary particles smaller than 2.5 microns (often written as $PM_{2.5}$) in urban areas. Combustion-generated particles are generally smaller than geologically produced dust and have unique chemical composition and morphology. The emission of particle matter that contains transition metals, ultrafine particles, and soot are controlled by the fuel composition and the oxidant-temperature-mixing history from the flame to the stack. Particle surface area, number of ultrafine particles, bioavailable transition metals, polycyclic aromatic hydrocarbon derivatives (PAH, also referred to as polynuclear aromatic hydrocarbon derivatives, PNAs), and other particle-bound organic compounds are important than particle mass in determining the effects of air pollution. Wood smoke forms when wood is combusted and is made up of a complex mixture of gases and fine particles (particulate matter, PM). In addition to particle pollution, wood smoke contains several toxic harmful air pollutants including benzene, formaldehyde, acrolein, and polycyclic aromatic hydrocarbon derivatives.

Aerosol particles have a lifetime of up to several weeks in the troposphere and occur in highly variable concentrations. A large proportion of the particles that influence cloud processes and the radiative balance is derived from gaseous sulfur-containing emissions.

See also: Pollution Control.

Agave Bagasse

Bagasse is the fibrous residue remaining after sugarcane or sorghum stalks are crushed to extract their juice and is currently used as a renewable resource in the manufacture of pulp and paper products and building materials. Bagasse is a heterogeneous material containing approximately 30-40% w/w of pith fiber, which is derived from the core of the plant and is mainly parenchyma material, and rind or stem fiber, which makes up the balance of the material. Bagasse is often used as a primary fuel source for sugar mills. When burned in quantity, it produces sufficient heat energy to supply all the needs of a typical sugar mill, with energy to spare. In addition, a secondary use for this waste product is in cogeneration, the use of a fuel source to provide both heat energy, used in the mill, and electricity, which is typically sold on to the consumer electrical grid.

Agave plants are used for fiber (henequén) production in the Yucatan peninsula for tequila and mezcal production in southern, west-central, and western Mexican states; and also for producing a traditional fermented beverage called pulque, in the highlands of central plateau of Mexico, including agricultural areas within the limits of Mexico City. The agave bagasse consists of the tissue of the blue agave after extraction of the sap. It is the residual fiber from slaughterhouses remaining after cooked agave heads are shredded and milled and the sugars are water-extracted. The bagasse is primarily the rind and fibrovascular bundles dispersed throughout the interior of the agave head.

The availability and characteristics of agave bagasse including structure, fiber size, and absorbency suggest that agave bagasse would be a suitable bulking agent for composting and to determine a viable method for the biodegradation of waste by piling alternate layers of offal with agave bagasse as a bulking agent.

See also: Bagasse, Biomass.

Agricultural Residue

Agricultural residues, which are a convenient renewable energy source, include straw, manure, vegetables, as well as fruit waste and general garden waste (Table A-5). Other residues include potatoes and sugar beet tops as well as damaged fruit and nursery wastes, and use of agricultural waste reduces the possibilities for odor and water pollution by manure. Aside from their abundance and renewability, using agricultural residues will benefit farmers, industry, and human health and the environment.

Table A-5 Examples of the Types and Bulk Composition of Agricultural Residues.

Agricultural residue	Cellulose	Hemicellulose	Lignin
Bagasse (sugar cane)	32-48	19-24	23-32
Bamboo	41-49	24-28	24-26
Cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Coastal Bermuda grass	25	35.7	6.4
Corn cobs	45	35	15
Corn stover	35	28	16-21
Grasses	25-40	35-50	10-30
Leaves	15-20	80-85	0
Nut shells	25-30	25-30	30-40
Pig waste	6.0	28	-
Rice straw	40	18	5.5
Sorghum (sweet)	27	25	11
Sorted refuse	60	20	20
Switch grass	30-51	10-50	5-20
Wastewater solids	8-15	NA	24-29
Wheat straw	33-40	20-25	15-20
Wood (hardwood)	40-50	24-40	18-25
Wood (softwood)	45-50	25-35	25-35

For example, until recently the excess straw produced was generally burned in the fields or ploughed back into the land. However, the environmental legislation put in place in many countries has restricted field burning and straw has been seen as a potential source of energy.

Dry residues include those parts of arable crops (such as corn stover, straw, and poultry litter) not to be used for the primary purpose of producing food, feed, or fiber, used in animal bedding and feathers. On the other hand, wet residues (which are residues and wastes that have a high water content as collected) include (i) animal slurry, (ii) farmyard manure, and (iii) grass silage.

Agriculture residues directly burned as fuel in the developing world include crop residues, forest litter, and also grass and animal garbage. Crop residues are more widely burnt than animal waste and forest litter. Crop residues encompass all agricultural wastes such as straw, stem, stalk, leaves, husk, shell, peel, lint, stones, pulp, stubble, etc. which come from cereals (rice, wheat, maize or corn, sorghum, barley, millet), cotton, groundnut, jute, legumes (tomato, bean, soy), coffee, cacao, olive, tea, fruits (banana, mango, coco, cashew), and palm oil.

Because agricultural residues are of a wide variety of types, the most appropriate energy conversion technologies and handling protocols vary from type to type. The most significant division is between those residues that are predominantly dry (such as straw) and those that are wet (such as animal slurry). Many agricultural crops and processes yield residues (Table A-6) that can potentially be used for energy applications, in a number of ways. Sources can include: (i) arable crop residues such as straw or husks, (ii) animal manures and slurries, and (iii) animal bedding such as poultry litter.

Table A-6 Examples of crops and crop wastes.

Crops	Crop wastes
Barley	Straw, bran
Coco	Hull, fiber
Coffee	Pulp, husk
Cotton	Stalk, lint, hull
Groundnut	Shell, stalk, leaves
Jute	Stem
Maize	Stalk, leaves
Mango	Peel
Millet	Straw, bran
Palm oil	Shell, fiber, fruit bunches
Rice	Straw, husk, bran
Sorghum	Straw, bran
Tomato	Stem
Wheat	Straw, husk, bran

Forest litter is mainly constituted of dry fallen leaves. Plantations of those species widely used for reforestation or soil conservation/sand fixation such as *Eucalyptus* and *Casuarina equisetifolia*, provide an important biomass litter yearly. Animal garbage is livestock manure. Generally, dry animal wastes directly used as fuel are cow and camel dung, and sometimes that of horse and sheep. The quantity of manure produced depends on the amount of fodder eaten, the quality of fodder, and the live weight of the animal. The excrement-yield values vary among the species.

In many developing countries, most agricultural residues burned as fuel are used in their natural state with some pre-treatment like drying, and cutting, and compacting in rare occasions. Crop residues are characterized by its seasonal availability and have characteristics that differ from other solid fuels such as wood, charcoal, and char briquette. The main differences are the high content of volatile matter and lower density and burning time.

The moisture content make wet residues energetically inefficient to use for combustion or gasification. It is preferable to process them close to production, and to use processes that can make use of biomass in an aqueous environment. Any moisture content must be driven off before processing (such as combustion) can take place, either in advance before storage or as part of the combustion process (which then uses part of the energy of the fuel). Gasification also requires relatively low moisture content (<10-15%).

Many of the above agricultural residues may have alternate uses or markets, and any decision to use them for energy must be made in the context of these renewable sources. In particular, many such residues are presently widely used for soil nutrient recycling and improvement purposes and may therefore be displacing significant quantities of synthetic fertilizers or other products. As the manufacture of many of these products entails significant carbon dioxide emissions and energy inputs, their substitution for agricultural residues should not be undertaken without caution.

See also: Agricultural Waste, Biomass, Residues, Rice Straw, Wheat Straw.

Agricultural Residue – Types

The four main types of agricultural residues are (i) feed and seed crop, (ii) fruit and nut crop, (iii) vegetable crop, and (iv) nursery crop and vary in composition (Table A-7).

Table A-7 Properties of various agricultural residues.

Agricultural residues	Volatiles (%)	Fixed carbon (%)	Ash (%)	HHV (Kj/kg)	LHV (Kj/kg)	Density (%)
Arhar stalk	83.47	14.76	1.77	15.00	14.85	
Bagasse	75.10	16.87	8.03	19.50	19.37	40 – 60
Bamboo dust	75.32	15.59	9.09	16.02	15.87	
Cotton stalk	70.89	22.43	6.68	18.26	17.85	10 – 20
Coconut coir	70.30	26.77	2.93	18.20	17.79	7 – 8
Corn cob	80.20	16.20	3.60	15.58	15.23	10 – 20
Dhaincha stalk	80.32	17.01	2.67	19.63	19.43	
Groundnut shell	68.12	24.97	6.91	17.20	17.06	
Jute stick	75.33	19.00	5.67	19.45	19.01	
Mustard shell	70.09	14.48	15.43	17.61	17.47	
Pine needle	72.38	26.12	1.50	20.12	19.97	
Rice husk	60.64	19.90	19.48	13.38	13.24	9
Sal seed leaves	60.03	20.22	19.75	18.57	18.42	
Sal seed husk	62.54	28.06	9.40	20.60	20.13	

Field and seed crop residues are the materials remaining above the ground after harvesting, including straw or stubble from barley, beans, oats, rice, rye, and wheat, stalks, or stover from corn, cotton, sorghum, soybeans, and alfalfa. The moisture content (wet basis) of these residues ranges from 8 to 80%. The typical bulk density of loose straw and stover varies from 1 to 3 lb/ft³ and the bulk density of baled straw and stover varies from 7 to 12 lb/ft³. If pelletized, the bulk density increases to 35 to 45 lb/ft³.

Fruit and nut crop residues include orchard pruning residues and brushes. The types of fruit and nut crops include almonds, apples, apricots, avocados, cherries, dates, figs, grapefruit, grapes, lemons, limes, olives, oranges, peaches, pears, plums, prunes, and walnuts. The moisture content (wet basis) of these residues ranges from 35 to 55%. Hammer-milled orchard pruning residues have a bulk density of from 9 to 12 lb/ft³.

Vegetable crop residues consist mostly of vines and leaves that remain on the ground after harvesting. The types of vegetable crops include such plants as artichokes, asparagus, cucumbers, lettuce, melon, potatoes, squash, and tomatoes. The moisture content (wet basis) of these residues is usually greater than 90%.

Nursery crop residues include the pruning residues and trimmings taken from the plants during their growth and in the preparation for market. There are more than 30 different species of nursery crops (such as flowers and indoor plants) that are grown. The moisture content of these residues is usually dependent on the type of crop that is being grown.

Quantifying the amounts and types of agricultural residues generated in each of the crop categories is extremely difficult, as it would require conducting comprehensive research throughout the state with continuous updates to the compiled data. Without ongoing data collection, any quantification estimates would only be valid for the time frame that the study was done and would be susceptible to ongoing market changes. Any quantification of agricultural residue tonnages should be viewed with these inherent limitations in mind and the tonnages quoted should not be considered absolute values.

See also: Agricultural Residues, Agricultural Waste, Residues, Rice Straw, Wheat Straw.

Agricultural Waste

Agricultural waste is the waste material remaining after processing crops to a marketable material or as a result of various agricultural operations. Agricultural wastes, which may include horticultural and forestry wastes, comprise crop residues, animal manure, diseased carcasses, as well as other wastes from farms, poultry houses and slaughterhouses, harvest waste, fertilizer run-off from fields, pesticides that enter into water, air, or soil; and salt and silt drained from fields.

The composition depends on the system of agriculture. Estimates of agricultural wastes are rare, but they are generally thought of as contributing a significant proportion of the total waste matter in the developed world. Since 1960, as a result of huge rises in productivity, there have been corresponding increases in the volumes of crop residues and animal manure requiring disposal. There is likely to be a significant increase in agricultural wastes globally if developing countries continue to intensify farming systems.

Agricultural wastes include both natural (organic) and non-natural waste materials. The main non-natural wastes include packaging, non-packaging plastics (such as silage and horticultural films); agrochemicals; animal health products (such as used syringes); waste from machinery (such as oil, tires, and batteries) and building waste (such as asbestos sheeting). Common wastes are sugar cane bagasse and cotton gin trash. Many agricultural wastes are sold as animal feed and materials unsuitable for use as animal feed are typically burned on site as fuel, thereby giving some processing plants the potential for being self-sufficient in energy.

See also: Agricultural Residues, Residues, Rice Straw, Wheat Straw.

Agrofuel

An agrofuel is a type of biofuel which is solid, liquid, or gaseous fuel and is obtained from relatively recently lifeless or living biological material. An agrofuel is a fuel that is obtained as a product of agriculture biomass and by-products at farming level, and/or industrial processing of raw material (agro-industries). The term covers mainly biomass materials derived directly from fuel crops and agro-industrial and animal by-products (Table A-8).

The three main types of biofuel are: (i) agrofuels, (ii) wood fuels, and (iii) municipal waste (sometime referred to as municipal by-products) which include gas, liquid, and solid products derived from processing activities (Table A-8) in which the major consideration is to identify the basic site where biomass production takes place. It is often necessary to distinguish whether the biofuel was connected to forest, agricultural, or municipal activities. The inclusion of a group on the use of agrofuels aims at distinguishing classical biofuels (generally related to forest exploitation) from those oriented toward annual or pluri-annual plantation.

Table A-8 Types of renewable fuel sources and products.

Source	Phase	Products
Agrofuels	Gas	Biogas, producer gas, pyrolysis gas from agrofuels
	Liquid	Ethanol, vegetable oil, methanol, pyrolysis oil
	Solid	Straw, stalks, husks, bagasse, charcoal
Woodfuels	Gas	Products from gasification and pyrolysis gases
	Liquid	Black liquor, methanol, pyrolysis oil
	Solid	Fuelwood (chips, sawdust, pellets), charcoal
Municipal waste	Gas	Landfill gas, sludge gas
	Liquid	Sewage sludge, pyrolysis oil
	Solid	Municipal solid waste

Another term – agrifuel – also referred to a fuel produced directly from crops and other agricultural sources. The term is also more generally applied to organic matter, converted to transportation fuels that reduce the use of imported oil and are more environmentally friendly.

Biodiesel is also an agrifuel that is blended with or replaces crude oil diesel. With biodiesel, any diesel engine can become a renewable fuel engine. Biodiesel is made in the USA from vegetable oils, animal fats, and used restaurant grease. Biodiesel is safer to use, handle, and store than crude oil diesel and is less environmentally damaging to produce, cleaner at the tailpipe (lower emissions), and less damaging if it spills on the ground or in water.

In addition, agricultural biodiesel (agri-biodiesel, agribiodiesel) is biodiesel produced from virgin vegetable oils derived from corn, soybeans, sunflower seeds, canola, cottonseeds, rapeseeds, safflowers, flaxseeds, rice bran, and mustard seeds, as well as from animal fats.

See also: Agrofuel, Biodiesel.

Air Emissions

Air emissions can arise from any one of several sources in any energy production plant, including: (i) combustion emissions associated with the burning of fuels, including fuels used in the generation of electricity, (ii) equipment leak emissions, which are also referred to (fugitive emissions) released through leaking valves, flanges, pumps, or other process devices, (iii) process vent emissions, which are also referred to as (point source emissions) released from process vents during manufacturing, (iv) storage tank emissions released when products are transferred to and from storage tanks, and (v) wastewater system emissions from tanks, ponds, and sewer system drains.

The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping, can be potential sources of sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon oxides (CO, CO₂), particulate matter, and volatile organic compounds, VOCs). When operating properly and when burning cleaner fuels such as natural gas, fuel gas, fuel oil, and process gas, these emissions are relatively low.

The three main greenhouse gases that are products of the various processes are carbon dioxide, nitrous oxide, and methane. Carbon dioxide is the main contributor to climate change. Methane is generally not as abundant as carbon dioxide but is produced during refining and, if emitted into the atmosphere, is a powerful greenhouse gas and more effective at trapping heat. However, gaseous emissions associated with biomass conversion to fuels typically include process gases, volatile organic compounds (VOCs), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH₃), and hydrogen sulfide (H₂S). These effluents may be discharged as air emissions and must be treated. However, gaseous emissions are more difficult to capture than wastewater or solid waste and, thus, are the largest source of untreated wastes released to the environment.

In addition to the corrosion of equipment by acid gases, the escape into the atmosphere of sulfur-containing gases can eventually lead to the formation of the constituents of acid rain, i.e., the oxides of sulfur (SO₂ and SO₃). Similarly, the nitrogen-containing gases can also lead to nitrous and nitric acids (through the formation of the oxides NO_x, where x = 1 or 2) which are the other major contributors to acid rain. The release of carbon dioxide and hydrocarbons as constituents of refinery effluents can also influence the behavior and integrity of the ozone layer.

Emissions from the sulfur recovery unit typically contain some hydrogen sulfide (H₂S), sulfur oxides, and nitrogen oxides. Other emissions sources from refinery processes arise from periodic regeneration of catalysts. These processes generate streams that may contain relatively high levels of carbon monoxide, particulates, and volatile organic compounds (VOCs). Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon monoxide boiler to burn carbon monoxide and any volatile organic compounds, and then through an electrostatic precipitator or cyclone separator to remove particulates.

The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems. In many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form.

See also: Acid Rain, Air Emissions, Pollutant.

Air Emissions – Biomass Plant

Biomass power plant emissions will be different from emissions from a coal-based power plant because biomass is lower in sulfur than most US coals. Typical biomass contains 0.05 to 0.20% w/w sulfur on a dry basis. In comparison, coal has 2 to 3% w/w sulfur on a dry basis. The biomass sulfur content translates to approximately 0.12 to 0.50 lb SO₂/MMBtu. Because of this, burning biomass to generate power typically produces less SO₂ emissions than using coal.

NO_x emissions should usually be lower for biomass than for coal, due to lower fuel nitrogen (N) content and due to the higher volatile fraction of biomass versus coal. However, this difference may not have much influence on the selection of the technology (i.e., coal or biomass) because the compliance costs are relatively insignificant given the small difference in NO_x emissions.

Biomass power production can result in large emissions of carbon dioxide (CO₂). Sometimes, biomass combustion results in larger emission values than for fossil fuels because of the lower combustion efficiencies. However, because the carbon dioxide released by combustion was removed from the atmosphere in the recent past through photosynthesis and new plant growth will continue to remove carbon dioxide from the atmosphere after biomass is harvested, it is sometimes argued that biomass is carbon dioxide neutral.

However, in practice, the issue is more complicated since other carbon flows are involved, including carbon dioxide emissions associated with fossil fuel used in harvesting, processing, and transportation operations. Although it is certain that the net amount of carbon dioxide emitted from a biomass power plant is less than a fossil power plant, it must be recognized that under current production practices, biomass power is not a net zero carbon dioxide process.

Biomass combustion device emissions are estimated on a site-specific basis to determine whether a particular location is appropriate for developing a facility. In many cases, data specific to a particular wood-burning appliance are not readily available. However, the United States Environmental Protection Agency provides emission factors that can be used to estimate emissions from wood-fired boilers as part of efforts to estimate the effects of specific combustion sources and determine the applicability of relevant permitting programs.

See also: Acid Rain, Air Emissions.

Air Flotation Processes

Air flotation processes are even more effective but are relatively complex. In the dissolved air flotation cell, air is injected into the oily wastewater as fine bubbles. The oil droplets adhere to the air bubbles and rise to the surface as a froth, which is skimmed off by a motor-driven rake. Some small, suspended particulate contaminants can also be removed in the froth, and others will settle to the bottom of the cell and can be removed as sludge. A coagulant can also be added to aid removal efficiency. If lime is added, for example, it will precipitate some heavy metals and certain anions such as carbonates.

Dissolved air flotation is a water treatment process that clarifies wastewaters (or other waters) by the removal of suspended matter such as oil or solids. The removal is achieved by dissolving air in the water or wastewater under pressure and then releasing the air at atmospheric pressure in a flotation tank or basin. The released air forms tiny bubbles which adhere to the suspended matter, causing the suspended matter to float to the surface of the water where it may then be removed by a skimming device.

Dissolved air flotation is very widely used in treating the industrial wastewater effluents from oil refineries, petrochemical and chemical plants, and natural gas processing plants and could find use in the oil shale industry.

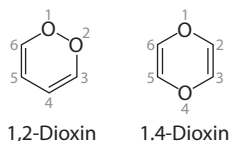
See also: Settling and Flotation.

Air Pollution

The term air pollution refers to the release of pollutants into the air that are detrimental to human health and the planet as a whole. Air pollution arises from energy use and production and not only from the use of fossil fuels but also from the use of fuels from renewable sources and also from natural events (using volcanoes as the example of a natural event). Air pollution may cause diseases, allergies, and even death to humans as well as cause harm to other living organisms such as animals and food crops, and may damage the environment.

Smog and soot are the most prevalent types of air pollution. The former (smog) occurs when emissions from the combustion of fuels (including biomass and other renewable fuel sources) react with sunlight. Soot (particulate matter) is composed of small (often micron-size) particles of chemicals, soil, smoke, dust, or allergens, in the form of gas or solids, that are carried in the air. Smog can irritate the eyes and throat and also damage the lungs – especially of people who work or exercise outside and is even worse for people who have asthma or allergies – the pollutants only intensify their symptoms and can trigger asthma attacks.

Hazardous air pollutants are either deadly or have severe health risks even in small amounts and most often emitted during gas or combustion of other fossil fuels and fossil fuel products. Polycyclic aromatic hydrocarbon derivatives are toxic components of traffic exhaust and wildfire smoke. In large amounts, they have been linked to eye and lung irritation, blood and liver issues, and even cancer. Dioxin derivatives are also present in small amounts in the air and can affect the liver in the short term and harm the immune, nervous, and endocrine systems, as well as reproductive functions.



Mold and allergens from trees, weeds, and grass are also carried in the air, are exacerbated by climate change, and can be hazardous to health. They are not regulated by the government and are less directly connected to human actions, but they can be considered air pollution. When homes, schools, or businesses are subject to water damage, mold can grow and can produce allergenic airborne pollutants. Exposure to mold can precipitate asthma attacks or an allergic response, and some molds can even produce toxins that would be dangerous for anyone to inhale. Pollen allergies are worsening because of climate change which extends the pollen production season.

See also: Gaseous Pollutants, Greenhouse Gases, Greenhouse Effect.

Alcohol Blended Fuel

Blended fuel usually refers to a mixture composed of automotive gasoline and another liquid, other than a minimal amount of a product such as carburetor detergent or oxidation inhibitor that can be used as a fuel in a motor vehicle.

Alcohol refers to ethyl alcohol (ethanol, C_2H_5OH), which has a high octane number, RON being 110, and MON 90 and a good antiknock performance. If alcohol contains a certain amount of water, it is favorable to improve its antiknock performance; hence, the enhancement of the compression ratio of the engine occurs when the blended fuel is burned. Meanwhile, an alcohol blend requires no or reduced additive of antiknock substance, which may reduce air pollution caused by lead (Pb). But the effect on increasing of the octane number of blended fuel is not the same when gasoline is mixed with different kinds of alcohol.

The data (Table A-9) show that the change in octane number of blended fuel is in nonlinear correlation with the proportion of alcohol added. A 5 to 20% alcohol blend has a higher mixed octane number. This means that the effect on raising the octane number of blend fuel is more notable. In addition, the lower the octane number of base gasoline is, the more notable the effect on raising the octane number of blended fuel will be.

Table A-9 Octane number (motor method).

Ethanol, % v/v	Octane number
0	72.5
5	74.8
10	76.6
15	78.5
20	80.3
25	81.4
100	90.0

Selecting a 15 to 20% blend of alcohol has the advantage of the high antiknock performance of the alcohol. However, if low octane gasoline is used as the base for the blend, without adding any antiknock fluid, not only can the pollution be reduced but the cost of fuel is decreased, thus making the use of mixed fuel on gasoline engine more adaptable.

See also: Blended Fuels.

Alcohol-Diesel Emulsion

Because alcohols have limited solubility in diesel, a stable emulsion must be formed that will allow it to be injected before separation occurs. Numerous techniques have been evaluated to allow for the concurrent use of diesel and ethanol in compression ignition engines. Some of these techniques include alcohol fumigation, dual injection, alcohol-diesel fuel emulsions, and alcohol-diesel fuel blends. Among these approaches, only alcohol-diesel *emulsions* and *blends* are compatible with most commercial diesel engines. Since emulsions are difficult to achieve and tend to be unstable, blends—either as micro-emulsions or using co-solvents—are the most common approach as they are stable and can be used in engines with relatively no modifications.

Blends of ethanol with diesel fuel are often referred to as E-Diesel or eDiesel or oxygenated diesel – a term that is not particularly precise since diesel blends containing methyl ester (biodiesel) or any other additive that includes oxygen can be also described as oxygenated diesel. In e-diesel blends, standard diesel fuel (such as US No. 2) is typically blended with up to 15% v/v of ethanol using an additive package that helps maintain blend stability and other properties such as the cetane number and the lubricity. The additive package may comprise from 0.2% to 5.0% v/v of the blend.

The use of e-diesel can bring some reductions in diesel PM emissions, while contradictory reports exist on its effect on nitrogen oxides, carbon monoxide, and emissions of hydrocarbon derivatives. Perhaps the biggest advantage of e-diesel is its partially renewable character, especially if renewable ethanol is used as the blending stock.

See also: Alcohols, Biodiesel, Butanol, Diesel Fuel, Ethanol, Hydroshear Emulsification, Methanol, Propanol.

Alcohol Fuels

Various alcohols ($C_nH_{2n+1}OH$) are used as fuel for internal combustion engines. The first four aliphatic alcohols (methanol, ethanol, propanol, and butanol) are of interest as fuels because they can be synthesized chemically or biologically, and they have characteristics which allow them to be used in internal combustion engines. When obtained from biological materials and/or biological processes, the alcohols are often referred to as bioalcohols (for example, bioethanol). However, there is no chemical difference between biologically produced and chemically produced alcohols.

Most methanol is produced from natural gas, although it can be produced from biomass using similar chemical processes. Ethanol is commonly produced from biological material through fermentation processes. Butanol has the advantage in combustion engines in that its energy density is closer to gasoline than the simpler alcohols (while still retaining over 25% higher octane rating). However, biobutanol is currently more difficult to produce than ethanol or methanol.

One advantage shared by the four major alcohol fuels is the high octane rating which tends to increase the fuel efficiency and largely offsets the lower energy density of vehicular alcohol fuels (as compared to gasoline and diesel fuels), thus resulting in comparable fuel economy in terms of distance per volume metrics, such as kilometers per liter, or miles per gallon.

See also: Alcohol-Blended Fuel.

Alcohol Fuels – Ethanol

Ethanol is the predominant fuel produced from crops that, because of favorable properties, has been used as fuel in the United States since at least 1908, along with methanol and gasoline (Table A-10).

Table A-10 Selected physical and chemical properties of methanol, ethanol, and gasoline.

Property	Methanol CH ₃ OH	Ethanol C ₂ H ₅ OH	Gasoline C4-C12
Molecular weight (g/mol)	32	46	~114
Specific gravity	0.789 (25°C, 77°F)	0.788 (25°C, 77°F)	0.739 (16°C, 60°F)
Vapor density rel. to air	1.10	1.59	3.0 (-40)
Liquid density (g/cm ³ at 25°C, 77°F)	0.79	0.79	3.0 to 4.0
Vapor pressure, 38°C (100°F)	4.6	2.5	8-10
Heat of evaporation (Btu/lb)	472	410	135
Heating value (kBtu gal ⁻¹)			
Lower (LHV)	58	74	111
Upper (UHV)	65	85	122
Viscosity (cp)	0.54	1.20	0.56
Flash point (°C, °F)	11 (52)	14 (57)	-36 (-33)
Flammability/explosion limits			
(%) Lower (LFL)	6.7	3.3	1.3
(%) Upper (UFL)	36	19	7.6

Although early efforts to sustain an ethanol program failed, oil supply disruptions in the Middle East and environmental concerns over the use of lead as a gasoline octane booster renewed interest in ethanol in the late 1970s. At present, extending the volume of conventional gasoline is a significant end use for ethanol, as is its use as an oxygenate. To succeed in these markets, the cost of ethanol must be close to the wholesale price of gasoline, currently made possible by the federal ethanol subsidy. However, in order for ethanol to compete on its own merits the cost of producing it must be reduced substantially.

The production of ethanol from corn is a mature technology that holds much potential. Substantial cost reductions may be possible, however, if cellulose-based feedstocks are used instead of corn. Producers are experimenting with units equipped to convert cellulose-based feedstocks, using sulfuric acid to break down cellulose and hemicellulose into fermentable sugar. Although the process is expensive at present, advances in biotechnology could decrease conversion costs substantially. The feed for all ethanol fermentations is sugar - traditionally a hexose (a six-carbon or "C6" sugar) such as those present naturally in sugar cane, sugar beet, and molasses. Sugar for fermentation can also be recovered from starch, which is actually a polymer of hexose sugars (*polysaccharide*).

Biomass, in the form of wood and agricultural residues such as wheat straw, is viewed as a low cost alternative feed to sugar and starch. It is also potentially available in far greater quantities than sugar and starch feeds. As such, it receives significant attention as a feed material for ethanol production. Like starch, wood and agricultural residues

contain polysaccharides. However, unlike starch, while the cellulose fraction of biomass is principally a polymer of easily fermented hexose (C6) sugars, the hemicellulose fraction is principally a polymer of pentose (C5) sugars; with quite different characteristics for recovery and fermentation, the cellulose and hemicellulose in biomass are bound together in a complex framework of crystalline organic material known as lignin.

These differences mean that recovery of these biomass sugars is more complex than recovery of sugars from a starch feedstock. Once recovered, fermentation is also more complex than a simple fermentation of hexose sugars. The current focus focuses on the issues of releasing the sugars (hydrolysis) and then fermenting as much of the C6 and C5 sugars as possible to produce ethanol.

There are several different methods of hydrolysis: (i) concentrated sulfuric acid, (ii) dilute sulfuric acid, (iii) nitric acid, and (iv) acid pretreatment followed by enzymatic hydrolysis.

Ethanol is produced from the fermentation of sugar by enzymes produced from specific varieties of yeast. The five major sugars are the five-carbon xylose and arabinose and the six-carbon glucose, galactose, and mannose. Traditional fermentation processes rely on yeasts that convert six-carbon sugars to ethanol. Glucose, the preferred form of sugar for fermentation, is contained in both carbohydrates and cellulose. Because carbohydrates are easier than cellulose to convert to glucose, the majority of ethanol currently produced in the United States is made from corn, which produces large quantities of carbohydrates. Also, the organisms and enzymes for carbohydrate conversion and glucose fermentation on a commercial scale are readily available.

The conversion of cellulosic biomass to ethanol parallels the corn conversion process. The cellulose must first be converted to sugars by hydrolysis and then fermented to produce ethanol. Cellulosic feedstocks (composed of cellulose and hemicellulose) are more difficult to convert to sugar than are carbohydrates. Two common methods for converting cellulose to sugar are dilute acid hydrolysis and concentrated acid hydrolysis, both of which use sulfuric acid.

Dilute acid hydrolysis occurs in two stages to take advantage of the differences between hemicellulose and cellulose. The first stage is performed at low temperature to maximize the yield from the hemicellulose, and the second, higher temperature stage is optimized for hydrolysis of the cellulose portion of the feedstock. Concentrated acid hydrolysis uses a dilute acid pretreatment to separate the hemicellulose and cellulose. The biomass is then dried before the addition of the concentrated sulfuric acid. Water is added to dilute the acid and then heated to release the sugars, producing a gel that can be separated from residual solids. Column chromatographic is used to separate the acid from the sugars.

Both the dilute and concentrated acid processes have several drawbacks. Dilute acid hydrolysis of cellulose tends to yield a large amount of by-products. Concentrated acid hydrolysis forms fewer by-products, but for economic reasons, the acid must be recycled. The separation and concentration of the sulfuric acid add more complexity to the process. The concentrated and dilute sulfuric acid processes are performed at high temperatures (100 and 220°C, 212 and 430°F) which can degrade the sugars, reducing the carbon source and ultimately lowering the ethanol yield. Thus, the concentrated acid process has a smaller potential for cost reductions from process improvements such as acid recovery and sugar yield for the concentrated acid process could provide higher efficiency for both technologies.

Another approach involves countercurrent hydrolysis, a two-stage process. In the first stage, cellulose feedstock is introduced to a horizontal co-current reactor with a conveyor. Steam is added to raise the temperature to 180°C (355°F; no acid is added at this point). After a residence time of approximately 8 minutes, during which some 60% of the hemicellulose is hydrolyzed, the feed exits the reactor. It then enters the second stage through a vertical reactor operated at 225°C (435°F). Very dilute sulfuric acid is added to the feed at this stage, where virtually all of the remaining hemicellulose and, depending on the residence time, anywhere from 60% w/w to all of the cellulose is hydrolyzed. The countercurrent hydrolysis process offers higher efficiency (and, therefore, cost reductions) than the dilute sulfuric acid process. This process may allow an increase in glucose yields to 84% w/w, an increase in fermentation temperature to 55°C (131°F), and an increase in fermentation yield of ethanol to 95% w/w.

The greatest potential for ethanol production from biomass, however, lies in enzymatic hydrolysis of cellulose. The enzyme cellulase, now used in the textile industry to stone wash denim and in detergents, simply replaces the sulfuric acid in the hydrolysis step. The cellulase can be used at lower temperatures, 30 to 50°C (86 to 122°F), which reduces the degradation of the sugar. In addition, process improvements now allow simultaneous saccharification and fermentation (SSF). In the saccharification and fermentation process, cellulase and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step. Once

the hydrolysis of the cellulose is achieved, the resulting sugars must be fermented to produce ethanol. In addition to glucose, hydrolysis produces other six-carbon sugars from cellulose and five-carbon sugars from hemicellulose that are not readily fermented to ethanol by naturally occurring organisms. They can be converted to ethanol by genetically engineered yeasts that are currently available, but the ethanol yields are not sufficient to make the process economically attractive. It also remains to be seen whether the yeasts can be made hardy enough for production of ethanol on a commercial scale.

A large variety of feedstocks is currently available for producing ethanol from cellulosic biomass. The materials being considered can be categorized as agricultural waste, forest residue, and energy crops. Agricultural waste available for ethanol conversion includes crop residues such as wheat straw, corn stover (leaves, stalks, and cobs), rice straw, and bagasse (sugar cane waste). Forestry waste includes underutilized wood and logging residues; rough, rotten, and salvable dead wood; and excess saplings and small trees. Energy crops, developed and grown specifically for fuel, include fast-growing trees, shrubs, and grasses such as hybrid poplars, willows, and switchgrass.

Briefly, corn stover is the leaves and stalks of field crops, such as corn (maize), sorghum, or soybean that are commonly left in a field after harvesting the grain. Corn stover is similar to straw, which is the residue left after any cereal grain or grass has been harvested at maturity for its seed and can be directly grazed by cattle or dried for use as fodder; stover has attracted some attention as a potential fuel source, and as a biomass feedstock for fermentation or as a feedstock for ethanol production from cellulose.

Although the choice of feedstock for ethanol conversion is largely a cost issue, feedstock selection has also focused on environmental issues. Materials normally targeted for disposal include forest thinnings collected as part of an effort to improve forest health, and certain agricultural residues, such as rice straw. Also, forest residues represent an opportunity to decrease the fire hazard associated with the dead wood present in many forests. Small quantities of forest thinnings can be collected at relatively low cost, but collection costs rise rapidly as quantities increase.

Agricultural residues, in particular corn stover, represent a tremendous resource base for biomass ethanol production. Agricultural residues, in the long term, would be the sources of biomass that could support substantial growth of the ethanol industry. At conversion yields of around 60 to 100 gal per dry ton, the available corn stover inventory would be sufficient to support 7 to 12 billion (7 to 12×10^9) gal of ethanol production per year.

Dedicated energy crops such as switchgrass, hybrid willow, and hybrid poplar are another long-term feedstock option. Switchgrass is grown on a 10-year crop rotation basis, and harvest can begin in year 1 in some locations and year 2 in others. Willows require a 22-year rotation, with the first harvest in year 4 and subsequent harvests every 3 years thereafter. Hybrid poplar requires 6 years to reach harvest age in the Pacific Northwest, 8 years in the Southeast, Southern Plains, and South Central regions, and 10 years in the Corn Belt, Lake States, Northeast and Northern Plains regions.

The use of cellulosic biomass in the production of ethanol also has environmental benefits. Converting cellulose to ethanol increases the net energy balance of ethanol compared to converting corn to ethanol. The net energy balance is calculated by subtracting the energy required to produce a gallon of ethanol from the energy contained in a gallon of ethanol (approximately 76,000 Btu). Corn-based ethanol has a net energy balance of 20,000 to 25,000 Btu per gallon, whereas cellulosic ethanol has a net energy balance of more than 60,000 Btu per gallon. In addition, cellulosic ethanol use can reduce greenhouse gas emissions. Cellulosic ethanol can produce an 8 to 10% reduction in greenhouse gas emissions when used in E10 and a 68 to 91% reduction when used in E85.

See also: Agricultural Residue, Agricultural Waste, Biomass, Alcohols.

Alcohol Fuels - Methanol

Alcohols are organic compounds that contain at least one hydroxyl functional group ($-\text{OH}$) bound to a saturate carbon atom. The term alcohol originally referred to the primary alcohol ethanol (ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{C}_2\text{H}_5\text{OH}$), which is used as a drug or as a relaxant-intoxicant in the form of alcoholic beverages. An important class of alcohols, of which methanol (methyl alcohol, CH_3OH) and ethanol are the simplest members, includes all compounds for which the general formula is $\text{C}_n\text{H}_{2n+1}\text{OH}$. Simple mono-alcohols (one hydroxyl group per molecule) include the primary alcohol derivatives (RCH_2OH), the secondary alcohol derivatives (R_2CHOH), and the tertiary alcohol derivatives (R_3COH) alcohols.

Methanol is a colorless, odorless, and nearly tasteless alcohol and is also produced from crops and is also used as a fuel. Methanol, like ethanol, burns more completely but releases as much or more carbon dioxide than its gasoline counterpart. The balance is often seen as the various bi-processes that draw carbon dioxide from the atmosphere so there is no net modern release, as there is for fossil fuels.

Methanol and other chemicals were routinely extracted from wood in the 19th Century and in the early 20th Century. However, the original route for methanol recovery from biomass was quite different to current routes. Methanol was originally recovered from wood as a by-product of charcoal manufacture, and was often called *wood alcohol*. Pyrolysis (heating wood in the absence of air) to above 270°C in a retort causes thermal cracking or break-down of the wood and allows much of the wood to be recovered as charcoal. The watery condensate leaving the retort contained methanol, among other compounds. In 1923, commercial production of methanol from synthesis gas by a catalytic process was commenced. Now, almost all of the methanol used worldwide comes from the processing of natural gas.

In general, methanol production from natural gas feed consists of three steps: (i) generation of synthesis gas – in the case of natural gas feed, synthesis gas production consists of converting methane (CH_4) into carbon monoxide (CO) and hydrogen (H_2) via steam reforming, (ii) synthesis gas upgrading - primarily removal of carbon dioxide, plus any contaminants such as sulfur, and (iii) methanol synthesis and purification - reacting the carbon monoxide, hydrogen, and steam over a catalyst in the presence of a small amount of carbon dioxide and at elevated temperature and pressure. The methanol synthesis is an equilibrium reaction, and excess reactants must be recycled to optimize yields.

Modern methods proposed for the production of methanol from biomass involve the conversion of the biomass to a suitable synthesis gas, after which processing steps are very similar to those developed for methanol from natural gas. However, the gasification techniques proposed are still at a relatively early stage of development using biomass feed and the methods are based on similar techniques used widely already with natural gas as feed.

Before biomass can be gasified, it must be pre-treated to meet the processing constraints of the gasifier. This typically involves size reduction, and drying to keep moisture contents below specific levels. Thereafter, biomass gasification involves heating biomass in the presence of low levels of oxygen (i.e., less than required for complete combustion to carbon dioxide and water). Above certain temperatures, the biomass will break down into a gas stream and a solid residue. The composition of the gas stream is influenced by the operating conditions for the gasifier, with some gasification processes more suited than others to producing a gas for methanol production. In particular, simple gasification with air creates a synthesis gas stream that is diluted with large quantities of nitrogen. This nitrogen is detrimental to subsequent processing to methanol, and so techniques using indirect gasification or an oxygen feed are preferred. For large-scale gasification, pressurized systems are considered to be more economic than atmospheric systems.

Once the economic optimum synthesis gas is available, the methanol synthesis takes place. This typically uses a copper-zinc catalyst at temperatures of 200 to 280°C and pressures of 50 to 100 atmospheres. The crude methanol from the synthesis loop contains water produced during synthesis as well as other minor by-products. Purification is achieved in multistage distillation, with the complexity of distillation dictated by the final methanol purity required.

See also: Alcohols.

Alcohol Fuels – Propanol and Butanol

Propanol and butanol are considerably less toxic and less volatile than methanol. In particular, butanol has a high flashpoint (35°C; 95°F), which is a benefit for fire safety, but may be a difficulty for starting engines in cold weather.

The fermentation processes to produce propanol and butanol from cellulose are fairly tricky to execute, and the *Clostridium acetobutylicum* currently used to perform these conversions produces an extremely unpleasant smell, and this must be taken into consideration when designing and locating a fermentation plant. This organism also dies when the butanol content of whatever it is fermenting rises to 7%. For comparison, yeast dies when the ethanol content of its feedstock reaches 14%. Specialized strains can tolerate even greater ethanol concentrations - so-called turbo yeast can withstand up to 16% ethanol. However, if ordinary *Saccharomyces* yeast can be modified to improve its ethanol resistance, scientists may yet one day produce a strain of the Weizmann organism with a butanol

resistance higher than the natural boundary of 7%. This would be useful because butanol has a higher energy density than ethanol, and because waste fiber left over from sugar crops used to make ethanol could be made into butanol, raising the alcohol yield of fuel crops without there being a need for more crops to be planted.

See also: Alcohols.

Alcohols

Alcohol is the family name of a group of organic chemical compounds composed of carbon, hydrogen, and oxygen and has fuel properties (Table A-11). The molecules in the series vary in chain length and are composed of a hydrocarbon plus a hydroxyl group. Alcohols are oxygenated fuels insofar as the alcohol molecule has one or more oxygen, which decreases to the combustion heat. Practically, any of the organic molecules of the alcohol family can be used as a fuel. The alcohols can be used for motor fuels are methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), and butanol ($\text{C}_4\text{H}_9\text{OH}$). However, only methanol and ethanol fuels are technically and economically suitable for internal combustion engines.

Table A-11 Fuel properties of methanol and ethanol compared to the properties of iso-octane.

Item	Iso-octane	Methanol	Ethanol
Formula	C_8H_{18}	CH_3OH	$\text{C}_2\text{H}_5\text{OH}$
Molecular weight	114.224	32.042	46.07
Carbon, % w/w	84.0	37.5	52.17
Hydrogen, % w/w	16.0	12.5	13.4
Oxygen, , % w/w	0	50.0	34.78
Boiling point @ 1 atmosphere °C	99.239	64.5	78.40
Freezing point @ 1 atmosphere °C	-107.378	-97.778	-80.00
Density @ 15.5 °C lb/gal	5.795	6.637	6.63
Viscosity @ 20°C, Centipoise	0.503	0.596	1.20
Specific heat @ 25°C/1 atm. Btu/lb	0.5	0.6	0.6
Heat of vaporization, @ boiling point/1 atm. Btu/lb	116.69	473.0	361.0
Heat of vaporization, @ 25°C/1 atm. Btu/lb	132.0	503.3	
Heat of combustion @ 25°C, Btu/lb			
Higher heating value	20555	9776	12780
Lower heating value	19065	8593	11550
Research octane number	100	106	105
Flash point, °C	-42.778	11.112	12.778
Auto-ignition temperature, °C	257.23	463.889	422.778
Flammability limits			
Lower	1.4	6.7	4.3
Higher	7.6	36.0	19.0

The alcohols are named accordingly to the basic molecules of hydrocarbon which derives from them: methanol (CH_3OH); ethanol ($\text{C}_2\text{H}_5\text{OH}$); propanol ($\text{C}_3\text{H}_7\text{OH}$); and butanol ($\text{C}_4\text{H}_9\text{OH}$), although menthol and ethanol are the most frequently used as fuel because of their distinguishing properties. Theoretically, any of the organic molecules of the alcohol family can be used as a fuel. The list is somehow more extensive; however, only two of the alcohols are technically and economically suitable as fuels for internal combustion engines. These alcohols are those of the simplest molecular structure, i.e., methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) (Table A-11).

Methanol is produced by a variety of process, the most common are as follows: distillation of wood; distillation of coal; natural gas; and crude oil gas. Ethanol is produced mainly from biomass transformation, or bioconversion. It can also be produced by synthesis from crude oil or mineral coal.

In those countries with large territorial areas, ethanol has been the renewable fuel choice to replace gasoline. The reason is the fact that alcohol is a renewable source of energy. Currently, ethanol is produced from sugar beets and from molasses - a typical yield is 15 to 20 gal of ethanol per ton of sugar cane. Other crops can be used for the production of ethanol. Corn, for example, can yield approximately 75 gal liters of alcohol.

Ethanol (ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$), also referred to as bioethanol, is a clear, colorless liquid with a characteristic, agreeable odor. Currently, the production of ethanol by fermentation of corn-derived carbohydrates is the main technology used to produce liquid fuels from biomass resources.

Ethanol can be blended with gasoline to create E85, a blend of 85% ethanol and 15% gasoline. Fuel with higher concentrations of ethanol (E95) and pure bioethanol (E100) has been used successfully in Brazil. More widespread practice has been to add up to 20% to gasoline (E20, also called gasohol) to avoid engine changes. E100-fueled and M100-fueled vehicles have difficulty starting in cold weather, but this is not a problem for E85 and M85 vehicles because of the presence of gasoline.

Ethanol has a higher octane number (108), broader flammability limit, higher flame speed, and a higher heat of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time, and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine. On the other hand, the disadvantages of ethanol include its lower energy density than gasoline, corrosiveness, low flame luminosity, lower vapor pressure, miscibility with water, and toxicity to ecosystems.

The alcohols mix in all proportions with water due to the polar nature of the hydroxyl (OH) group. Low volatility is indicated by high boiling point and high flash point. Alcohols burn with no luminous flame, and methanol produces almost no soot, but the tendency to produce soot increases with molecular weight.

See also: Alcohols – Production, Ethanol, Methanol.

Alcohols – Combustion

There are some important differences in the combustion characteristics of alcohols and hydrocarbon derivatives. Alcohols have higher flame speeds and extended flammability limits. Also, alcohols produce a great number of product moles per mole of fuel burnt; therefore, higher pressure is achieved.

The alcohols mix in all proportions with water due to the polar nature of OH group. Low volatility is indicated by high boiling point and high flash point. Alcohols burn with no luminous flame and produce almost no soot, especially methanol. The tendency to soot formation increases with molecular weight.

Combustion of alcohol in presence of air can be initiated by an intensive source of localized energy, such as a flame or a spark, and also, the mixture can be ignited by application of energy by means of heat and pressure, such as happens in the compression stroke of a piston engine. The energy of the mixture reaches a level sufficient for ignition to take place after a brief period of delay called ignition delay, or induction time, between the sudden heating of the mixture and the onset of ignition (formation of a flame front which propagates at high speed throughout the whole mixture). The high latent heat of vaporization of alcohols cools the air entering the combustion chamber of the engine, thereby increasing the air density and mass flow. This leads to increased volumetric efficiency and reduced compression temperatures. Together with the low level of combustion temperature, these effects also improve the thermal efficiency by 10%.

Alcohols have higher flame speeds and extended flammability limits than hydrocarbons. Also, alcohols produce a great number of product moles per mole of fuel burnt; therefore, higher pressure is achieved. The higher flame speed, giving earlier energy release in the power stroke, results in a power increase of 11% at normal conditions and up to 20% at the higher levels of a compression ratio (14:1). The power continues to rise steadily as the mixture is enriched to an equivalence ratio of approximately 1 to 4. Because of the low proportion of carbon in alcohols, soot formation does not occur and therefore alcohols burn with low luminosity and therefore low radiation. In conjunction with lower flame temperature, approximately 10% less heat is lost to the engine coolant. The lower flame temperature of alcohols results in much lower NO_x (nitrogen oxides) emissions. The wider flammability limits of alcohols permit smooth engine operation even at very lean mixtures. But aldehyde emissions are noticeably higher. For ethanol, emissions are acetaldehydes, and for methanol, emissions are of formaldehydes. Increasing compression ratio from 9 to 14, aldehyde emissions can be reduced by 50%, to a level compared to that for gasoline. An addition of 10% water reduces aldehyde emissions by 40% and NO_x by 50%. Addition of 10% water in the alcohol can be tolerated without loss of thermal efficiency.

The oxygen content of alcohols depresses the heating value of the fuel in comparison with hydrocarbon fuels. The heat of combustion per unit volume of alcohol is approximately half that of isooctane. However, the stoichiometric fuel-air mass ratios are such big that the quantity of energy content based on unit mass of stoichiometric mixture becomes comparable with that of hydrocarbon derivatives.

Methanol is not miscible with hydrocarbon derivatives, and separation ensues readily in the presence of small quantities of water, particularly with reduction in temperature. Anhydrous ethanol, on the other hand, is completely miscible in all proportions with gasoline, although separation may be affected by water addition or by cooling. If water is already present, the water tolerance is higher for ethanol than for methanol, and can be improved by the addition of higher alcohols, such as butanol.

The high heat of vaporization and constant boiling point make cold starting difficult with neat alcohols. The problem is not as severe as in case of alcohols blended with gasoline. Ethanol has a constant boiling point of 80°C (176°F). Gasoline which has a high vapor pressure (therefore highly volatile) can be used for cold start.

See also: Alcohols, Butanol, Ethanol, Methanol, Propanol.

Alcohols – Corrosivity

Dry methanol is very corrosive to some aluminum alloys, but additional water at 1% almost completely inhibits corrosion. It must be noted that methanol with additional water at more than 2% becomes corrosive again. The same happens with less than 1% water. Nitride and neoprene rubbers, generally satisfactory as elastomers in contact with methanol and polyacetal plastics, are very resistant. Silicon rubber as well as vinyl can be used for gasket material. Ethanol always contains acetic acid and is particularly corrosive to aluminum alloys. Also, certain alloys containing lead are attacked with a general result of the lead being leached out, leaving a porous surface. The same phenomenon exists with alloys of zinc, such as ZAMAC (zinc plus aluminum), and the zinc is leached out as a white zinc oxide, which clogs the small orifices and jets.

Carburetors are normally made of ZAMAC alloy. Experience has shown that if the carburetor is protected with a coat of nickel, the corrosion problem is overcome. The process recommended is electrolysis nickel plating. In this process, the carburetor parts are immersed in a bath of hot nickel, which, due to the low viscosity, covers evenly all the surfaces without clogging the orifices. The floats on the carburetor float-bowl are generally made of porous plastics which are attacked by the ethanol, and the end result is swelling and cracking. It is found that nylon floats are more durable. A float can be made with thin sheet of brass (0.005 in) or 0.125 mm thickness, molded and welded with pure tin (Sn).

Alloys of tin and lead (Sn+ Pb) shall be avoided as welding material. All bronze parts shall be brass or stainless steel. Steel fuel lines shall be replaced by nylon tube (Nylon 11). Fuel filters used for gasoline are not recommended for the many alcohols. The internal element collapses after the glue that bonds it together is softened by the alcohol. Special filters are necessary. Also, due to the higher flows, filters have to be bigger. The filter body must be made of nylon or Teflon.

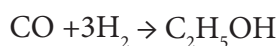
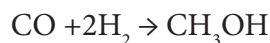
See also: Alcohols, Butanol, Ethanol, Methanol, Propanol.

Alcohols – From Waste

Alcohols can be made from organic materials by fermentation, and there is the potential for the production of alcohols from organic waste. Historically, the production of methanol, ethanol, and higher molecular alcohols from syngas has been known since the beginning of the 20th century. There are several processes that can be used to make mixed alcohols from synthesis gas including iso-synthesis, variants of Fischer-Tropsch synthesis, oxo-synthesis involving the hydroformylation of olefins, and homologation of methanol and lower molecular weight alcohols to make higher alcohols. In the context of the Fischer-Tropsch process, depending on the process and its operating conditions, the most abundant products are usually methanol and carbon dioxide, but methanol can be recycled to produce higher molecular weight alcohols.

With the development of various gas-to-liquid processes, it was recognized that higher alcohols were by-products of these processes when catalysts or conditions were not optimized. Modified Fischer-Tropsch (or methanol synthesis) catalysts can be promoted with alkali metals to shift the products toward higher alcohols. Synthesis of higher molecular weight alcohols is optimal at higher temperatures and lower space velocities compared to methanol synthesis and with a ration of hydrogen/carbon monoxide ratio of approximately 1 rather than 2 or greater.

In the process, the feedstock enters the process and is converted to synthesis gas with the desired carbon monoxide/hydrogen ratio, which is then reacted, in the presence of a catalyst, into methanol (CH₃OH), ethanol (CH₃CH₂OH), and higher molecular weight alcohols.



Thus,



Stoichiometry suggests that the carbon monoxide/hydrogen ratio is optimum at 2, but the simultaneous presence of water-gas shift leads to an optimum ratio closer to 1.

As in other synthesis gas conversion processes, the synthesis of higher molecular weight alcohols generates significant heat and an important aspect is choice of the proper reactor to maintain even temperature control which then maintains catalyst activity and selectivity. In fact, the synthesis of higher molecular weight alcohols is carried out in reactors similar to those used in methanol and Fischer-Tropsch synthesis. These include shell and tube reactors with shell-side cooling, trickle-bed, and slurry bed reactors.

Catalysts for the synthesis of higher molecular weight alcohols generally fall mainly into four groups: (1) modified high pressure methanol synthesis catalysts, such as alkali-doped ZnO/Cr₂O₃, (2) modified low pressure methanol catalysts, such as alkali-doped Cu/ZnO and Cu/ZnO/Al₂O₃, (3) modified Fischer-Tropsch catalysts, such as alkali-doped CuO/CoO/Al₂O₃, and (4) alkali-doped sulfides, such as mainly molybdenum sulfide (MoS₂).

The catalytic synthesis process makes several different alcohols depending, in part, on residence time in the reactor and the nature of the catalyst. The alcohols can be separated by distillation and dried to remove water.

A further aspect of the waste-to-alcohols concept is the use of a plasma field (<http://www.fuelfrontiers.com/technology.htm>) in which temperatures are reputed (but not yet proved) to reach 30,000°C (54,000°F). The feedstock can be materials such as waste coal, used tires, wood wastes, raw sewage, municipal solid wastes, biomass, discarded roofing shingles, coal waste (*culm*), and discarded corn stalks. The plasma field breaks down the feedstock into their core elements in a clean and efficient manner.

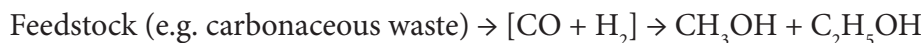
See also: Alcohols.

Alcohols – Production

Alcohols can be produced from a variety of feedstocks. For example, ethanol is produced from organic feedstocks, such as biomass, by a fermentation process. However, recent efforts have focused on the production of ethanol

from waste materials using a gasification process. The overall process consists of a thermochemical conversion of synthesis gas which is then converted to higher molecular weight alcohols by a catalytic process, after which high purity ethanol is separated by distillation. The process is similar to the methanol and gas-to-liquid process. The key differentiating factors are the catalysts and their operating parameters.

Alcohols can be made directly from organic feedstocks (such as sugars and sugar derivatives) by fermentation or indirectly by the production of synthesis gas, and there is the potential for the production of alcohols from organic waste.

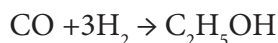
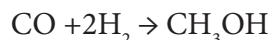


synthesis gas methanol ethanol

Historically, the production of methanol, ethanol, and higher molecular alcohols from synthesis gas has been known since the beginning of the 20th century. There are several processes that can be used to make mixed alcohols from synthesis gas including iso-synthesis, variants of Fischer-Tropsch synthesis, oxo-synthesis involving the hydroformylation of olefins, and homologation of methanol and lower molecular weight alcohols to make higher alcohols. In the context of the Fischer-Tropsch process, depending on the process and its operating conditions, the most abundant products are usually methanol and carbon dioxide, but methanol can be recycled to produce higher molecular weight alcohols.

With the development of various gas-to-liquid processes, it was recognized that higher alcohols were by-products of these processes when catalysts or conditions were not optimized. Modified Fischer-Tropsch (or methanol synthesis) catalysts can be promoted with alkali metals to shift the products toward higher alcohols. Synthesis of higher molecular weight alcohols is optimal at higher temperatures and lower space velocities compared to methanol synthesis and with a hydrogen/carbon monoxide ratio of approximately 1 rather than 2 or greater.

In the process, the feedstock enters the process and is converted to synthesis gas with the desired carbon monoxide/hydrogen ratio, which is then reacted, in the presence of a catalyst, into methanol (CH₃OH), ethanol (CH₃CH₂OH), and higher molecular weight alcohols.



Thus,



Stoichiometry suggests that the carbon monoxide/hydrogen ratio is optimum at 2, but the simultaneous presence of water-gas shift leads to an optimum ratio closer to 1.

As in other synthesis gas conversion processes, the synthesis of higher molecular weight alcohols generates significant heat and an important aspect is choice of the proper reactor to maintain even temperature control which then maintains catalyst activity and selectivity. In fact, the synthesis of higher molecular weight alcohols is carried out in reactors similar to those used in methanol and Fischer-Tropsch synthesis. These include shell and tube reactors with shell-side cooling, trickle-bed, and slurry bed reactors.

Catalysts for the synthesis of higher molecular weight alcohols generally fall mainly into four groups: (i) modified high pressure methanol synthesis catalysts, such as alkali-doped ZnO/Cr₂O₃, (ii) modified low pressure methanol catalysts, such as alkali-doped Cu/ZnO and Cu/ZnO/Al₂O₃, (iii) modified Fischer-Tropsch catalysts, such as alkali-doped CuO/CoO/Al₂O₃, and (iv) alkali-doped sulfides, such as mainly molybdenum sulfide (MoS₂).

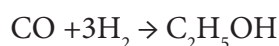
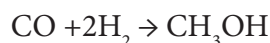
The catalytic synthesis process makes several different alcohols depending, in part, on residence time in the reactor and the nature of the catalyst. The alcohols can be separated by distillation and dried to remove water.

A further aspect of the waste-to-alcohols concept is the use of a plasma field in which temperatures are reputed (but not yet proved) to reach 30,000°C (54,000°F). The feedstock can be materials such as waste coal, used tires, wood wastes, raw sewage, municipal solid wastes, biomass, discarded roofing shingles, coal waste (culm), and discarded corn stalks. The plasma field breaks down the feedstock into their core elements in a clean and efficient manner.

Most efforts for alcohol production have centered on bacteria, enzyme, and acid/solvent hydrolysis fermentation-based ethanol production. However, the action of bacteria and enzymes is often very dependent on the feedstock. In addition, these processes generate a small quantity of ethanol over a period of days and the dilute aqueous ethanol product must be distilled to recover the ethanol. In the gasification-synthesis process, various carbonaceous feedstocks can be used, with appropriate modifications in the synthesis gas production step.

A new system for converting trash into ethanol and methanol could help reduce the amount of waste piling up in landfills while displacing a large fraction of the fossil fuels used to power vehicles in the United States. The technology developed does not incinerate refuse, so it does not produce the pollutants that have historically plagued efforts to convert waste into energy. Instead, the technology vaporizes organic materials to produce synthesis gas that can be used to synthesize a wide variety of fuels and chemicals. In addition to processing municipal waste, the technology can be used to create ethanol out of agricultural biomass waste, providing a potentially less expensive way to make ethanol than current corn-based plants.

The new system makes synthesis gas in two stages. In the first stage, waste is heated in a 1,200°C (2,190°F) chamber into which a controlled amount of oxygen is added to partially oxidize carbon and free hydrogen. Not all of the organic material is converted, and some forms char which is then gasified when researchers pass it through arcs of plasma. The remaining inorganic materials, including toxic substances, are oxidized and incorporated into a pool of molten glass which hardens into a material that can be used for building roads or discarded as a safe material in landfills. The second stage is a catalyst-based process for converting synthesis gas into equal ethanol and methanol.



Ethanol from cellulosic biomass materials (such as agricultural residues, trees, and grasses) is made by first using pretreatment and hydrolysis processes to extract sugars, followed by fermentation of the sugars. Although producing ethanol from cellulosic biomass is currently more costly than producing ethanol from starch crops, several countries (including the United States) have launched biofuel initiatives with the objective of the economic production of ethanol from bio-sources. In the process, the carbohydrate from the biomass is converted to a sugar derivative; this is converted to ethanol in a fermentation process that is similar to the process for brewing beer; typical feedstocks for the process are sugar beets and from molasses.

Ethanol can also be produced by synthesis from the chemical compound ethylene, which is derived from crude oil or natural gas, or by the fermentation of carbohydrates.

Methanol (methyl alcohol, wood alcohol, CH_3OH) is mainly manufactured from natural gas, but biomass can also be gasified to methanol. Methanol can be made with any renewable resource containing carbon such as seaweed, waste wood, and garbage. Methanol is stored and handled like gasoline because it is produced as a liquid. Methanol is currently made from natural gas, but it can also be made from a wide range of renewable biomass sources, such as wood or waste paper.

Methanol can be used as one possible replacement for conventional motor fuels and, like ethyl alcohol, has a high octane rating; hence an Otto engine is preferable. If an ignition booster is used, methanol can be used in a diesel engine.

Methanol also offers important emissions benefits compared with gasoline. It can reduce hydrocarbon emissions by 30 to 40% with M85 and up to 80% with M100 fuels. Methanol costs less than gasoline, but has lower energy content. Taking this into account, costs for methanol in a conventional vehicle are slightly higher than those for gasoline.

However, methanol is not miscible with hydrocarbon derivatives and separation ensues readily in the presence of small quantities of water, particularly with reduction in temperature. Anhydrous ethanol, on the other hand, is completely miscible in all proportions with gasoline, although separation may be effected by water addition or by

cooling. If water is already present, the water tolerance is higher for ethanol than for methanol, and can be improved by the addition of higher alcohols, such as butanol. Also, benzene or Acetone can be used.

See also: P-Series Fuels.

See also: Alcohols.

Algaculture

Algaculture is a form of aquaculture involving the farming of species of algae. The majority of algae that are intentionally cultivated fall into the category of microalgae (also referred to as phytoplankton, microphytes, or planktonic algae).

Macroalgae (seaweed) also have many commercial and industrial uses, but due to their size and the specific requirements of the environment in which they need to grow, they do not lend themselves as readily to cultivation. However, as the algae grow and multiply, the culture becomes so dense that it blocks light from reaching deeper into the water. Direct sunlight is too strong for most algae, which need only approximately 10% of the amount of light they receive from direct sunlight.

Algae can be cultured in open-ponds which are vulnerable to contamination by other microorganisms, such as other algal species or bacteria. Thus cultivators usually choose closed systems for monocultures. Open systems also do not offer control over temperature and lighting. The growing season is largely dependent on location and, aside from tropical areas, is limited to the warmer months.

Open pond systems are cheaper to construct, at the minimum requiring only a trench or pond. Large ponds have the largest production capacities relative to other systems of comparable cost. Open pond cultivation can exploit unusual conditions that suit only specific algae and can also work if there is a system of culling the desired algae and inoculating new ponds with a high starting concentration of the desired algae.

Enclosing a pond with a transparent or translucent barrier effectively turns it into a greenhouse. This allows more species to be grown; it allows the species that are being grown to stay dominant; and it extends the growing season – and if heated, the pond can produce year round.

Algae can also be cultured in a photobioreactor (PBR) which is a bioreactor that incorporates a light source. However, because photobioreactor systems are closed, the cultivator must provide all nutrients, including carbon dioxide. A photobioreactor can operate in batch mode, which involves restocking the reactor after each harvest, but it is also possible to grow and harvest continuously. Continuous operation requires precise control of all elements to prevent immediate collapse. The grower provides sterilized water, nutrients, air, and carbon dioxide at the correct rates. This allows the reactor to operate for long periods.

See also: Algae, Algae Fuels.

Algae

Algae are a large and diverse group of simple, typically autotrophic organisms, ranging from unicellular to multicellular forms. The largest and most complex marine forms are called seaweeds, which are photosynthetic but lack the many distinct organs found in land plants. Microalgae are organisms that are less than 0.4 mm in diameter and include the diatoms and cyanobacteria and are capable of photosynthesis. Macroalgae are organisms such as seaweed.

Algae are not highly differentiated in the way that plants are, and they lack true roots, stems and leaves, and a vascular system to circulate water and nutrients throughout their bodies. They can exist as single, microscopic cells; they can be macroscopic and multicellular; live in colonies; or take on a leafy appearance as in the case of seaweeds.

The general term algae includes prokaryotic organisms cyanobacteria, also known as blue-green algae, as well as eukaryotic organisms (all other algal species). Algae lack the various structures that characterize land plants, such as leaves, roots, and other organs that are found in vascular plants. Many algae are photoautotrophic, although some groups contain members that are mixotrophic, deriving energy both from photosynthesis and uptake of organic

carbon. Some unicellular species rely entirely on external energy sources and have limited or no photosynthetic apparatus.

The majority of algae live in aquatic habitats and these organisms can thrive in freshwater lakes or in saltwater oceans. They can also endure a range of temperatures, oxygen or carbon dioxide concentrations, acidity, and turbidity. An important contribution of algae to the environment and well-being is the generation of oxygen through photosynthesis.

Algal biofuels are a promising replacement for fossil fuels. All algae have the ability to produce energy-rich oils, and several microalgal species naturally accumulate high levels of oil in their dry mass. Moreover, algae are found in diverse habitats and can reproduce quickly and also efficiently use carbon dioxide. Algae help to keep atmospheric carbon dioxide levels stable by storing carbon dioxide in organic materials that include crude oil and inorganic carbonate rocks. Green algae, diatoms, and cyanobacteria are just some of the microalgal species that are considered good candidates for the production of biofuel.

See also: Algae Fuel, Aquatic Plants, Biomass.

Algae Fuels

Algae fuel is a biofuel that is derived from algae, which are photosynthetic, eukaryotic, plant-like organisms that use chlorophyll in capturing light energy, but lack characteristic plant structures such as leaves, roots, flowers, vascular tissue, and seeds. The production of algae to harvest oil for biofuels has not yet been undertaken on a commercial scale. But algae potentially can be grown commercially in environments such as algae ponds at wastewater treatment plants and the oil extracted from the algae and processed into biofuels. During photosynthesis, algae and other photosynthetic organisms capture carbon dioxide.

The benefits of algal biofuel are that it can be produced industrially, thereby obviating the use of arable land and food crops (such as soy, palm, and canola), and that it has a high yield of oil when compared to other sources of biofuel. Thus, algaculture, unlike food crop-based biofuels, does not entail a decrease in food production, since it requires neither farmland nor fresh water.

Algae can produce up to 60% of their biomass in the form of oil. Because the cells grow in aqueous suspension where they have more efficient access to water, carbon dioxide, and dissolved nutrients, microalgae are capable of producing large amounts of biomass and usable oil in either high rate algal ponds or photobioreactors. This oil can then be turned into biodiesel. In fact, seaweeds, which are macroscopic, multicellular marine algae, may offer a particular useful source of biofuels, since they lack lignin and likewise do not require land, fresh water, or fertilizer. One complication is that approximately one-third of the sugars in seaweed take the form of alginate and microbes have not been able to convert it into ethanol.

In the process of oil production, the algae is harvested from the growing process as algae paste after which water is removed by heat drying or de-watering presses. Centrifuges are also another way in which the algae past can be de-watered. The finished product is algae oil in a form that is then suitable for use in the transesterification process to make biodiesel fuel.

The production of biofuel from algae does not reduce atmospheric carbon dioxide (CO_2), because any carbon dioxide taken out of the atmosphere by the algae is returned when the biofuels are burned. They do however eliminate the introduction of new carbon dioxide by displacing fossil hydrocarbon fuels. Also, algal fuels do not affect fresh water resources and they can be produced using ocean and wastewater. Algal fuels are also biodegradable and relatively harmless to the environment if spilled.

Open-pond systems for the most part have been given up for the cultivation of algae with high-oil content. Open systems using a monoculture are also vulnerable to viral infection. The energy that a high-oil strain invests into the production of oil is energy that is not invested into the production of proteins or carbohydrates, usually resulting in the species being less hardy, or having a slower growth rate. Algal species with lower oil content, not having to divert their energies away from growth, have an easier time in the harsher conditions of an open system.

The preference toward microalgae is due largely to its less complex structure, fast growth rate, and high oil content (for some species). Some commercial interests into large scale algal-cultivation systems are looking to tie in to existing infrastructures, such as coal power plants or sewage treatment facilities. This approach not only provides the raw

materials for the system, such as carbon dioxide and nutrients; it also changes those wastes into resources. However, there is interest in using seaweed for biofuels, probably due to the high availability of this resource.

Algae fuel is also very appealing in terms of its emissions as well. The combustion of algae fuel produces less carbon monoxide, unburned hydrocarbons, and harmful pollutants compared to crude oil-derived diesel fuel as well as emits no sulfur oxides. Replacing fossil fuels with algae could substantially reduce carbon dioxide emissions.

In addition, microalgae has a strong impact on wastewater, and systems for producing microalgae have the ability of being able to use saline waste, as well as carbon dioxide streams, as an energy source. This is because the algae from microalgae bioreactors is capable of capturing organic compounds and heavy metal contaminants in wastewater. As a result, the production of algae has the side effect of being able to recycle formerly unusable water. In fact, not only does this process clean waste water, but it also recovers phosphorus from the waste water. Phosphorus is a highly limited resource, so much so that the last reserves of phosphorus are estimated to have already been depleted.

Biogasoline is gasoline produced from biomass such as algae. Like traditionally produced gasoline, the constituents contain between 6 carbon atoms (hexane, C_6H_{14}) and 12 (dodecane, $C_{12}H_{26}$) carbon atoms per molecule and can be used in internal-combustion engines. Biogasoline is chemically different from biobutanol and bioethanol, as these are alcohols, not hydrocarbons.

See also: Algae, Aquatic Plants, Biomass.

Algae Fuels – Extraction

Algae fuels can be recovered by three processes: (i) physical extraction or (ii) chemical extraction, and (iii) enzymatic extraction.

In the first step of physical extraction, the oil must be separated from the rest of the algae. The simplest method is mechanical crushing. When algae are dried it retains its oil content, which can then be recovered using an oil press. Many commercial manufacturers of vegetable oil use a combination of mechanical pressing and chemical solvents in extracting oil. Since different strains of algae vary widely in their physical attributes, various press configurations (such as the screw, expeller, and piston configurations) work better for specific algae types. Often, mechanical crushing is used in conjunction with chemical solvents.

Ultrasonic extraction is a type of physical extraction that can greatly accelerate extraction processes. Using an ultrasonic reactor, ultrasonic waves are used to create cavitation bubbles in a solvent material. When these bubbles collapse near the cell walls, the resulting shock waves and liquid jets cause those cells walls to break and release their contents into a solvent. Ultrasonication can enhance basic enzymatic extraction. The combination sono-enzymatic treatment accelerates extraction and increases yields.

In chemical extraction, chemical solvents are often used in the extraction of the oils. A common choice of chemical solvent is hexane, although other hydrocarbon solvents can also be used. Another method of chemical solvent extraction is Soxhlet extraction in which oils from the algae are extracted through repeated washing, or percolation, with an organic solvent, under reflux in specialized equipment. The value of this technique is that the solvent is reused for each cycle.

Supercritical carbon dioxide can also be used as a solvent. In this method, carbon dioxide is liquefied under pressure and heated to the point that it becomes supercritical (having properties of both a liquid and a gas), allowing it to act as a solvent.

Enzymatic extraction uses enzymes to degrade the cell walls with water acting as the solvent. This makes fractionation of the oil much easier. The enzymatic extraction can be supported by ultrasonication.

See Algae, Algae Fuels, Aquatic Plants, Biomass.

Algal Blooms

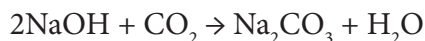
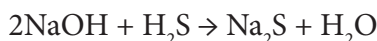
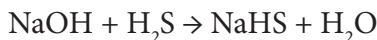
Algal blooms refer to the rampant growth of certain microalgae, which in turn leads to the production of toxins, disruption of the natural aquatic ecosystems, and increases the costs of water treatments. The blooms take on the colors of the algae contained within them. Graham states that the main toxin producers in oceans are certain dinoflagellates

and diatoms. In freshwaters, cyanobacteria are the main toxin producers, though some eukaryotic algae also cause problems. Under natural conditions, Graham notes that algae use the toxins to protect themselves from being eaten by small animals and only need a small amount to protect themselves.

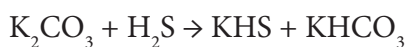
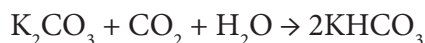
The main cause of algal blooms is nutrient pollution in which there is an excess of nitrogen and phosphorus, which can push algae toward unrestrained growth. The phenomenon is caused by a variety of human activities in which the fertilizers used in agriculture and animal manures are rich in nitrogen, while improperly treated wastewater is high in both nitrogen and phosphorus.

Alkali Washing Process

Alkali washing (often referred to as caustic scrubbing) for hydrogen sulfide removal with caustic scrubbing is only economical in small amounts if hydrogen sulfide is present and suitable means of disposing the spent solution are available. The chemistry is simple and to some extent, depending upon the concentration of hydrogen sulfide in the gas stream, efficient. Thus:



Carbonate washing is a mild alkali process for emission control by the removal of acid gases (such as carbon dioxide and hydrogen sulfide) from gas streams and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature. It has been demonstrated that the process works best near the temperature of reversibility of the reactions:



In the Benfield process, acid gases are scrubbed from the feed in an absorber column using potassium carbonate solution with Benfield additives to improve performance and avoid corrosion.

Water washing, in terms of the outcome, is analogous to washing with potassium carbonate (Kohl and Riesenfeld, 1985), and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical, and there is also a relatively high absorption of hydrocarbon derivatives, which are liberated at the same time as the acid gases.

See also: Gas Cleaning, Gas Processing, Gas Treating, Hot Potassium Carbonate Process, Scrubbing.

Alicyclic Hydrocarbons

Alicyclic hydrocarbons contain cyclic structures in all or part of the chemical skeleton. The saturated alicyclic hydrocarbons have the general formula C_nH_{2n} . When the molecular formula of a saturated hydrocarbon corresponds to the general formula $\text{C}_n\text{H}_{2n-2}$, then the compound contains two rings; if the formula corresponds to $\text{C}_n\text{H}_{2n-4}$, it contains three rings, etc. Their boiling points and densities are higher than alkanes having the same number of carbon atoms. In crude oil, the most frequently found rings are those having five or six carbon atoms. In these rings, each hydrogen atom can be substituted by a paraffinic alkyl chain that is either a straight chain or branched. Monocyclic naphthenes with one ring are major constituents of the light fraction. Monocyclic naphthene of carbon numbers C_{20} to C_{30} , with long side chains can be isolated from paraffin waxes.

Cycloalkanes (naphthenes) catalytically crack by both ring and chain rupture and yield olefins and paraffin. In the case of hydrocracking process, polycyclic hydrocarbons aromatic are partially hydrogenated. Naphthene rings in polycyclic compounds are readily removed by ring-opening followed by cracking. Single-ring naphthenes and paraffin are more resistant to cracking. It was also found that single-ring naphthenes appear to react more slowly at high conversion levels. In the catalytic reforming process, the fundamental reaction occurring is (i) dehydrogenation of six members rings naphthenes by platinum catalyst, and (ii) isomerization of alkyl cyclopentane derivatives to cyclohexane derivatives.

The stability of the cycloalkane derivatives increases up to the six member ring, then decreases from seven to eleven member ring, and from the twelve member onwards attains the stability of two six member rings (Table A-12).

Table A-12 Properties of selected alicyclic hydrocarbon derivatives.

Alicyclic hydrocarbon (naphthene)	Melting point, °C	Boiling point, °C	Density, @20 °C
Cyclopropane	-127	-33	
Cyclobutane	-80	13	
Cyclopentane	-94	49	0.746
Cyclohexane	6.5	81	0.778
Cycloheptane	-12	118	0.810
Cyclooctane	14	149	0.830
Methylcyclopentane	-142	72	0.749
Cis-1,2- dimethylcyclopentane	-62	99	0.772
Trans-1,2- dimethylcyclopentane	-120	92	0.750
Methylcyclohexane	-126	100	0.769

Aliphatic Hydrocarbons

Aliphatic hydrocarbon derivatives (also known as paraffins or paraffin derivatives) are straight chain or branched saturated organic compounds with composition $C_n H_{2n+2}$. Paraffin derivatives are present in large amounts in nature and low molecular weight paraffin derivatives are found in natural gas. Methane is the lowest member of the paraffin series of hydrocarbons. With the increase in size of molecule, several hydrocarbons may exist. Such hydrocarbons have different properties and are known as isomers. On the other hand, olefin hydrocarbon derivatives have carbon atoms joined by two bonds.

Hydrocarbon derivatives are classified into chemical families according to their structure. All structures are members of the homologous series of even hydrogen numbers. The chemical formula is $C_n H_{2n+2}$ or lower in hydrogen content $C_n H_{2n}$. The carbon-carbon molecule chains have different chemical bonding arrangements such as (i) saturated hydrocarbon derivatives that are linked by carbon-carbon single bonds and are given the suffix *ane* and (ii) unsaturated hydrocarbon derivatives that are linked by multiple bonds double bond $C=C$ (suffix *ene*) or triple $C\equiv C$ (suffix *yne*). However, the same molecule can contain several multiple bonds – if there are two low sets of the double bond, the suffix is *diene*.

Normal alkanes (straight-chain paraffins) consist of a chain of carbon atoms. Each carbon atom is linked to four atoms, which can be either carbon or hydrogen, their general formula $C_n H_{2n+2}$. The carbon skeleton can be structured as straight chains as are the normal paraffin, $CH_3(CH_2)_n CH_3$. The boiling points increase with the number of carbon atoms. With the low carbon numbers, the addition of a carbon increases the boiling point to approximately 25°C. Further additions give smaller increase. At the same time, the density increases with the molecular weight 0.626 kg/L for pentane, and 0.791 kg/L for pentacosane; on the other hand, the density is always much lower than 1. The normal alkanes from C_1 to C_4 are colorless gases; C_5 to C_{17} colorless liquids; and from C_{18} onwards, colorless solids. Other physical properties, such as melting point, density, and viscosity, also increase in the same way as boiling point (Table A-13). There is a relationship between physical properties and chemical composition. The variation in boiling point of compounds is due to different intermolecular forces such as hydrogen bonding. The alkanes are insoluble in water.

Table A-13 Physical properties of n-paraffins.

Alkane	Melting point, °C	Boiling point, °C	Density, g/ml @20°C
Methane	-183	-162	
Ethane	-172	-88.5	
Propane	-167	-42	
Butane	-138	0	
Pentane	-130	36	0.626
Hexane	-95	69	0.659
Heptane	-90	98	0.684
Octane	-57	126	0.703
Nonane	-54	151	0.718
Decane	-30	174	0.730
Undecane	-26	196	0.740
Dodecane	-10	216	0.749
Tridecane	-6	234	0.757
Tetradecane	5.5	252	0.764
Pentadecane	10	266	0.769
Hexadecane	18	280	0.775
Heptadecane	22	292	
Octadecane	28	308	
Nonadecane	32	320	

Isoparaffins (Table A-14) are paraffins in which branching is present, usually at the number 2 carbon atom, although branching can take place at a different position in the chain, although such molecules are not strictly isoparaffins. Isoparaffins (branched paraffins) have a boiling point lower than normal paraffin with same number of carbon atoms, and generally, the greater the branching, the lower the boiling point (Table A-14).

Table A-14 Physical properties of selected branched paraffins.

Paraffin	Melting point, °C	Boiling point, °C	Density, g/ml @20 °C
Isobutane	-159	-12	
Isopentane	-160	28	0.620
Neopentane	-17	9.5	
Isohexane	-154	60	0.654
3-Methylbutane	-118	63	0.676
2,2-Dimethylbutane	-98	50	0.649
2,3-Dimethylbutane	-129	58	0.668

Octane number is a measure of the ability of a fuel (gasoline) to avoid knocking. The test engine is adjusted to give knock from the fuel rated. Then, various mixtures of isooctane (2,2,4-trimethylpentane) and n-heptane are used to find the ratio of the two reference fuels that will give the same intensity knock as that from unknown fuel. Defining isooctane as having an octane number of 100 and n-heptane as 0, the octane number is the volumetric percentage of isooctane in heptane that matches knock from the unknown fuel is reported as octane number of the fuel.

Unsaturated aliphatic hydrocarbon derivatives (olefin derivatives) (Table A-15) have one or more double bonds between carbon atoms. Also, olefin derivatives have different types of isomers – for example, butene (C_4H_8) isomers have many arrangements which include 1-butene ($CH_3CH_2CH=CH_2$), cis 2-butene (cis- $CH_3CH=CHCH_3$), trans 2-butene (trans- $CH_3CH=CHCH_3$), and isobutene [$(CH_3)_2CH=CH_2$].

Table A-15 Physical properties of selected olefins.

Olefin	Melting point, °C	Boiling point, °C	Density, g/ml @20°C
Ethylene	-169	-102	
Propylene	-158	-48	
1-Butene		-6.5	
1-Pentene		30	
1-Hexene	-138	63.5	0.643
1-Heptene	-119	93	0.675
1-Octene	-104	122.5	0.698
1-Nonene		146	0.716
1-Decene	-87	171	0.731
Cis-2-butene	-139	4	0.743
Trans-2-butene	-106	1	
Isobutylene	-141	-7	
Cis-2-pentene	-151	37	
2-Methyl-2-butene	-123	39	0.655
2,3-Dimethyl-2-butene	-74	73	0.660
Cyclopentene	-93	46	0.705
Cyclohexene	-104	83	0.774
1,3-Cyclopentadiene	-85	42	0.810
1,3-Cyclohexadiene	-49	87	0.798
			0.847

Owing to the presence of a double bond, the alkene undergoes a large number of addition reactions, but under special conditions, they also undergo substitution reactions. Alkene is readily hydrogenated under pressure in the presence of a catalyst. Platinum and palladium are effective at room temperature. Addition polymerization occurs between molecules containing double or triple bonds. The following are some reactions of aliphatic hydrocarbons to enhance its properties.

See also: Alkanes, Alkenes.

Alkalinity

Alkalinity is a measure of the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. Alkalinity is closely related to the acid neutralizing capacity (ANC) of a solution, and it is the acid neutralizing capacity that is often incorrectly used to refer to alkalinity.

The alkalinity of a system is equal to the stoichiometric sum of the bases in solution. In the natural environment, carbonate alkalinity tends to make up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of carbon dioxide in the atmosphere.

Alkalinity is sometimes incorrectly used interchangeably with basicity as when the pH of a solution can be lowered by the addition of carbon dioxide. This will reduce the basicity; however, the alkalinity will remain unchanged.

Alkaloids

Alkaloids are a class of nitrogenous organic compounds of plant origin which have pronounced physiological actions on humans and include many drugs (morphine, quinine) and poisons (atropine, strychnine). Alkaloids are naturally occurring chemical compounds containing basic nitrogen atoms and are produced by a large variety of organisms, including bacteria, fungi, plants, and animals.

The alkaloids are perhaps the last class of organic compounds which originate in plants that are of any importance in the formation of the organic substance of coal. These compounds all contain basic nitrogen in the molecule with the nitrogen frequently occurring in a cyclic system; in addition, most of the alkaloids also contain oxygen functions.

Alkaloids are biologically active, organic compounds that contain a nitrogen atom which compounds have many structural frameworks, and are therefore highly variable. Alkaloids occur in the roots, bark, leaves, and within the cells of many plants. The structural chemistry of the alkaloids is variable because of the many locations in which nitrogen can occur in organic systems. However, it is generally recognized that the alkaloids may be based on any one of several individual (or even on a combination of two or more) systems.

Alkaloids are divided into the several large groups, such as pyrrolidine, pyridine, quinoline, isoquinoline, indole, and quinazoline. They are often divided into main groups including peptides and cyclopeptide alkaloids, and true-alkaloids, proto-alkaloids, polyamine-alkaloids, and pseudo-alkaloids. Although most alkaloids are pharmacologically active or poisonous in high doses, there are some alkaloids in foods that are often consumed daily, of which the common examples are caffeine, theobromine, and theophylline (members of the purine alkaloid family) which are mainly found in coffee, cocoa beans, and tea leaves.

Alkaloids have been isolated as crude extracts from plants for many millennia as part of folk medications. However, since the 20th Century, individual alkaloids with defined and scientifically verified pharmacological properties have been purified and produced commercially as fine chemicals.

The complexity of the chemical structures of the alkaloids makes them, in most cases, impossible to produce by chemical synthesis, so extraction from a crude plant mixture remains the most economically viable strategy. However, plants normally produce complex mixtures of alkaloids (rather than a single alkaloid) with the desirable types often at low levels, with the result that commercially produced specific alkaloids are expensive. As the genetic manipulation of plants becomes more sophisticated, research has focused on the engineering of alkaloid biosynthesis to generate transgenic or cell lines that overproduce specific alkaloids. This can be achieved by increasing the synthesis of a particular alkaloid and/or inhibiting the synthesis of related compounds to increase the ease of purification.

Alkanes

Alkanes (sometimes referred to as paraffins or paraffin hydrocarbons) are aliphatic hydrocarbons (non-aromatic hydrocarbon derivatives) that contain carbon and hydrogen only in which all of the binding orbitals of the carbon atoms are satisfied by bonding to another carbon atom or to a hydrogen atom.

Normal alkanes (straight-chain paraffins) consist of a chain of carbon atoms. Each carbon atom is linked to four atoms, which can be either carbon or hydrogen, their general formula C_nH_{2n+2} (Table A-16). The carbon skeleton can be structured as straight chains as are the normal paraffin, $CH_3(CH_2)_nCH_3$. The boiling points increase with the number of carbon atoms. With the low carbon numbers, the addition of a carbon increases the boiling point by approximately 25°C (77°F). Further additions give smaller increase. At the same time, the density increases with the molecular weight 0.626 kg/L for pentane, and 0.791 kg/L for pentacosane; on the other hand, the density is always much lower than 1. The normal alkanes from C_1 to C_4 are colorless gases; C_5 to C_{17} colorless liquids; and from C_{18} onwards, colorless solids. Other physical properties, such as melting point, density, and viscosity, also increase in the same way as boiling point. There is a relationship between physical properties and chemical composition. The variation in the boiling point of compounds is due to different intermolecular forces such as hydrogen bonding. The alkanes are insoluble in water.

Table A-16 Physical properties of n-paraffins.

Alkane	Melting point, °C	Boiling point °C	Density, g/ml @20°C
Methane	-183	-162	
Ethane	-172	-88.5	
Propane	-167	-42	
Butane	-138	0	
Pentane	-130	36	0.626
Hexane	-95	69	0.659
Heptane	-90	98	0.684
Octane	-57	126	0.703
Nonane	-54	151	0.718
Decane	-30	174	0.730
Undecane	-26	196	0.740
Dodecane	-10	216	0.749
Tridecane	-6	234	0.757
Tetradecane	5.5	252	0.764
Pentadecane	10	266	0.769
Hexadecane	18	280	0.775
Heptadecane	22	292	
Octadecane	28	308	
Nonadecane	32	320	

Isoparaffins are paraffins in which branching is present, usually at the number 2 carbon atom, although branching can take place at a different position in the chain, although such molecules are not strictly isoparaffins. Isoparaffins have a boiling point lower than normal paraffin with same number of carbon atoms, and generally, the greater branching has the lower boiling point (Table A-17).

Table A-17 Physical properties of selected branched paraffins.

Paraffins	Melting point, °C	Boiling point, °C	Density, g/ml @20 °C
Isobutane	-159	-12	
Isopentane	-160	28	0.620
Neopentane	-17	9.5	
Isohexane	-154	60	0.654
3-Methylbutane	-118	63	0.676
2,2-Dimethylbutane	-98	50	0.649
2,3-Dimethylbutane	-129	58	0.668

The octane number is a measure of the ability of a fuel (gasoline) to avoid knocking. The test engine is adjusted to give knock from the fuel rated. Then, various mixtures of isooctane (2,2,4-trimethylpentane) and n-heptane are used to find the ratio of the two reference fuels that will give the same intensity knock as that from unknown fuel. Defining isooctane as 100 octane number and n-heptane as 0, the octane number is the volumetric percentage of isooctane in heptane that matches knock from the unknown fuel is reported as the octane number of the fuel.

Alkanolamines

The removal of acid gases by the alkanolamine process (*amine process*) is accomplished by a chemical reaction. Physical solvents (Selexol, Sulfinol, Propylene Carbonate) remove acid gases by straight absorption or a combination of absorption and chemical reaction.

The alkanolamine can be categorized on a chemical basis as being primary (MEA, DGA), secondary (DEA, DIPA), and tertiary (MDEA, TEA) depending on the number of substitutions onto a central nitrogen atom. Solvents currently in use include formulated MDEA (Ucarsol, Gas Spec) and hindered amines (FLEXSORB). This chemical structure influences each properties of the alkanolamine as a treating solvent and therefore, lend themselves to different applications.

Furthermore, the following is a list of conditions must be defined when selecting a treating solvent: (i) the operating pressure and temperature, (ii) the amount of acid gases and quantity removed, selectivity, and treated gas specifications, (iii) the disposal of the acid gases such as sulfur recovery and/or incineration, (iv) the contaminants in the inlet gas, such as oxygen, mercaptans and other sulfur species, free liquids, and gas composition, and (v) the environment, such as spill reporting and allowable ambient sulfur oxide emission.

Alkazid Process

The Alkazid process is a process for the removal of hydrogen sulfide and carbon dioxide from gas streams using concentrated aqueous alkaline (caustic) solutions of amino acids. The process is used primarily to treat gas of high sulfur content before it goes to other stops for more complete purification. It also claimed the advantage of yielding hydrogen sulfide of high concentration of up to 90% hydrogen sulfide. The process has been used to treat gas containing up to 10% v/v hydrogen sulfide and removes the hydrogen sulfide to 0.07 to 0.10% v/v. The process is also used for low pressure CO₂ removal where sulfur is not present or is present in small quantities.

In the process, the purified gas stream leaves the unit from the top of the absorber or absorbers and the cold lean alkaline solution passes countercurrent to the gas down the columns, out the bottom through a screen and is pumped through a heat exchanger countercurrent to the hot lean caustic from the bottom of the stripper. From the heat exchanger, the rich alkaline solution is fed to the top of the stripper column. The stripper kettle temperature is maintained at approximately 105°C (220°F). The stripped gas (hydrogen sulfide and carbon dioxide) leaves the top of the stripper, and passes through a condenser and separator to remove condensate, thence out of the system to the Claus Unit or other disposal system.

The steam to heat the kettle of the stripper is distributed between direct and indirect heating in order to hold the specific gravity of the alkaline solution between 1.16 and 1.20. If the gravity of the solution gets too high or the solution gets too cold, solids will settle out. The stripped caustic leaves the bottom of the absorber through a screen, passes through the countercurrent heat exchange mentioned above, through a water cooler and to the top of the absorber.

There are two types of solutions used in the Alkazid process: (i) the DIK caustic version – the solution most commonly used – is a solution of potassium dimethyl or diethyl alpha amino-acetate and is used to remove hydrogen sulfide from gases containing carbon disulfide, and (ii) the M-caustic version which uses a solution of potassium methyl alpha amino-propionate which absorbs both hydrogen sulfide and carbon dioxide but is used only in the absence of carbon disulfide. The usual effective gas charge of the solutions ranges from 10 to 15 volumes per volume of caustic for best removal of hydrogen sulfide but can be increased to as much as 30 to 35 volumes per volume by use of mechanical contacting devices and longer contact time, or by permitting higher sulfur content in the outlet gas.

Absorption and stripping are at substantially atmospheric pressure, and the optimum absorption temperature is approximately 5°C (41°F), but a temperature up to 30°C (86 °F) can be used satisfactorily. The relative absorption of carbon dioxide by the DIK-caustic version increases with increased absorption temperature, and with increased time of contact over the normal 1 minute. Any oxygen that enters the system during the operation forms thiosulfates in the solution, destroying its effectiveness. Special precautions are taken to prevent air entering the system at pump packing, or in the solution storage vessels, etc. This difficulty limits the use of the process to oxygen-free gases.

Alkenes

An alkene (olefin) is an unsaturated chemical compound containing at least one carbon-to-carbon double bond (Table A-18). The simplest acyclic alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n} . The simplest alkene is ethylene (C_2H_4), which has the International Union of Pure and Applied Chemistry (IUPAC) name ethene. Alkenes are also called olefins (an archaic synonym, widely used in the petrochemical industry).

The physical properties of alkenes are comparable with those of alkanes (aliphatic hydrocarbons). The physical state depends on molecular mass (gases from ethylene to butene - liquids from pentene onwards). The simplest alkenes, ethylene, propylene (propene), and butylene (butene) are gases. Linear alkenes of approximately 5 to 16 carbons are liquids, and higher molecular weight alkenes are waxy solids. Alkenes are more reactive than alkanes due to the presence of a carbon-carbon pi-bond (double bond). The majority of the reactions of alkenes involve the rupture of this pi bond, forming new single bonds.

Table A-18 Physical properties of selected olefins.

Olefin	Melting point, °C	Boiling point, °C	Density, g/ml @20 °C
Ethylene	-169	-102	
Propylene	-158	-48	
1-Butene		-6.5	
1-Pentene		30	
1-Hexene	-138	63.5	0.643
1-Heptene	-119	93	0.675
1-Octene	-104	122.5	0.698
1-Nonene		146	0.716
1-Decene	-87	171	0.731
Cis-2-butene	-139	4	0.743
Trans-2-butene	-106	1	
Isobutylene	-141	-7	
Cis-2-pentene	-151	37	
2-Methyl-2-butene	-123	39	0.655
2,3-Dimethyl-2-butene	-74	73	0.660
Cyclopentene	-93	46	0.705
Cyclohexene	-104	83	0.774
1,3-Cyclopentadiene	-85	42	0.810
1,3-Cyclohexadiene	-49	87	0.798
			0.847

Alkenes serve as a feedstock for the petrochemical industry because they can participate in a wide variety of reactions.

The simplest acyclic alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n} .

The physical properties of alkene derivatives are comparable with those of alkane derivatives (aliphatic hydrocarbon derivatives). The physical state depends on molecular mass (gases from ethylene to butene and liquids from pentene onwards). The simplest alkenes, ethylene, propylene (propene), and butylene (butene) are gases. Linear alkenes of approximately 5 to 16 carbons are liquids, and higher molecular weight alkenes are waxy solids.

Alkene derivatives are more reactive than alkane derivatives due to the presence of a carbon-carbon pi-bond (double bond). The majority of the reactions of alkenes involve the rupture of this pi bond, forming new single bonds.

Alpha Decay

Alpha decay (α -decay) is the radioactive emission of an α -particle which is the nucleus of helium-4 (^4He), consisting of two protons and two neutrons which is a stable nucleus as it is doubly magic. The daughter nucleus has two protons and four nucleons fewer than the parent nucleus. In general, alpha decay leads to the ground state of the daughter nucleus so that the emitted particle carries away as much energy as possible.

By way of definition, a nucleon is either a proton or a neutron considered in its role as a component of an atomic nucleus. The number of nucleons in a nucleus defines the mass number (the nucleon number) of an isotope. In fact, protons and neutrons are best known in their role as nucleons, i.e., as the components of atomic nuclei, but they also exist as free particles. Free neutrons are unstable, with a half-life of approximately 13 minutes, but they have important applications. Protons not bound to other nucleons are the nuclei of hydrogen atoms when bound with an electron or – if not bound to anything – are ions or cosmic rays. Both the proton and the neutron are composite particles insofar as each is composed of smaller parts and, thus, neither the proton nor the neutron is an elementary particle.

A pertinent example from the area of nuclear energy is the decay of uranium-238 (^{238}U) to thorium-234 (^{234}Th). An alpha particle (also called alpha rays or alpha radiation) has a charge of $+2e$, but, as a nuclear equation, describes a nuclear reaction without considering the electrons and consists of two protons and two neutrons bound together into a particle identical to a helium-4 (^4He) nucleus and are typically the product of the alpha decay process. The symbol for the alpha particle is α or α^{2+} , and because alpha particles are identical to helium nuclei, they are also sometimes written as He^{2+} or $^4_2\text{He}^{2+}$ which indicates a helium ion with a +2 charge (missing two electrons). Once the ion gains electrons from its environment, the alpha particle becomes a normal (electrically neutral) helium atom ^4_2He .

Alpha decay typically occurs in the heaviest nuclides, and, theoretically, it can occur only in nuclei somewhat heavier (higher atomic number) than nickel atomic (number = element 28), where the overall binding energy per nucleon is no longer a minimum and the nuclides are therefore unstable toward spontaneous fission-type processes. In practice, this mode of decay has only been observed in nuclides considerably heavier than nickel, with the lightest known alpha emitters being the lightest isotopes (mass numbers 104 to 109) of tellurium (atomic number = element 52).

When an atom emits an alpha particle in alpha decay, the mass number of the atom decreases by four due to the loss of the four nucleons in the alpha particle. The atomic number of the atom decreases by two, as a result of the loss of two protons, and the atom becomes a new element. Also, unlike other types of decay, alpha decay as a process must have a minimum-size atomic nucleus that can support it. The process may leave the nucleus in an excited state after which the emission of a gamma ray then removes the excess energy.

See also: Beta Decay, Gamma Decay, Nuclear Energy.

Alpha Particle

An alpha particle (also termed alpha radiation or alpha rays) is a helium nucleus stripped of its orbital electrons and which is emitted from a radioactive atom with a velocity of about 1/20 that of the speed of light and with energies ranging from 4 to 9 MeV. The alpha particle was the first nuclear radiation to be discovered; beta particles and gamma rays were identified soon thereafter.

Alpha particles cause ionizations in matter when they are deflected by the positive charge of a nucleus and pull the orbital electrons (attracted by the alpha's positive charge) along with them. Alpha particles also cause excitation along their path by pulling inner orbital electrons to outer orbits. Energy is then given off by the atom as fluorescent radiation (low energy x-rays) when the electrons drop back down to the inner orbital vacancies.

Because of its relatively large mass (2 neutrons and 2 protons), high electrical charge (2+) and low velocity, the specific ionization of an alpha particle is high and, as a result, it creates many ion pairs in a very short path length. Because of this, it loses all of its energy in a short distance. The range in air is only several centimeters even for the most energetic alpha particles.

Alpha particles are highly ionizing because of the double positive charge, large mass (compared to a beta particle), and because they are relatively slow. They can cause multiple ionizations within a short distance which gives

alpha particles the potential to do much more biological damage for the same amount of deposited energy. Alpha particles cannot penetrate the normal layer of dead cells on the outside of our skin but can damage the cornea of the eye. Alpha-particle radiation is normally only a safety concern if the radioactive decay occurs from an atom that is already inside the body or a cell. Alpha-particle emitters are particularly dangerous if inhaled, ingested, or if they enter a wound. Once inside the body, surrounded by living tissue, damage will be to the local area in which the alpha emitter is deposited. Thus, alpha emitters are an internal hazard and intake to the body must be prevented.

See also: Beta Decay, Beta Particle, Gamma Decay, Nuclear Energy.

Alternate Fuels

Alternate fuels (renewable fuels, advanced fuels, synthetic fuels which include liquid and gaseous fuels, as well as clean solid fuels) are any materials or substances that can be used as fuels, other than conventional fuels. Alternate fuels are derived from resources such as coal, oil shale, or tar sands, and various forms of biomass – in the last case the term that is more appropriate is renewable fuels. Renewable fuels are making headway into the fuel balance by reducing dependence on imported oil. Often, renewable fuels produce less pollution than crude oil-derived gasoline or crude oil-derived diesel fuel.

Examples of renewable fuels and renewable energy sources are: (i) biodiesel, which is diesel fuel derived from vegetable oils and animal fats. It usually produces less air pollutants than crude oil-based diesel, (ii) biogas which is produced from the anaerobic digestion of diverse organic waste sources using various methods, (iii) biomass liquids: produced by biomass-to-gas-to-liquid conversion and by pyrolysis processes which involve the conversion of biomass, such as wood and agricultural residues, (iv) ethanol or other alcohols produced domestically from corn and other crops and produces less greenhouse gas emissions than conventional fuels, and (v) hydrogen which is produced from biomass, (vi) nuclear power, or (vii) other sources such as solar energy, tidal energy, and wind energy and hydroelectric power.

Biodiesel from plant sources is similar to diesel, but has differences that include higher cetane rating (45 to 60 compared to 45 to 50 for crude oil-derived diesel fuel), and it acts as a cleaning agent to get rid of dirt and deposits. As with alcohols and gasoline engines, taking advantage of the high cetane number of biodiesel potentially overcomes the energy deficit compared to ordinary number 2 diesel.

See also: Biodiesel, Biogas, Hydrogen, Synthetic Fuel.

Alternate Fuels – Gaseous Fuels

Gaseous fuels are those fuels that are in the gaseous state under ambient conditions. In some circumstances, the definition of gaseous fuels may also include the low-boiling hydrocarbons such as pentane but such fuels are considered to be liquid fuels.

Biogas (i.e., gas from biological or alternate sources) is a clean and renewable form of energy, and the most important biogas components are methane (CH_4), carbon dioxide (CO_2), and sulfuric components (H_2S). The gas is generally composed of methane (55 to 65%), carbon dioxide (35 to 45%), nitrogen (0 to 3%), hydrogen (0 to 1%), and hydrogen sulfide (0 to 1%). Biogas could very well substitute for conventional sources of energy (i.e., fossil fuels) which are causing ecological–environmental problems and at the same time depleting at a faster rate. Due to its elevated methane content, resultant of the organic degradation in the absence of molecular oxygen, biogas is an attractive source of energy. The physical, chemical, and biological characteristics of the manure are related to diet composition, which can influence the biogas composition. Raw natural gas is approximately 70 to 95% methane, but biogas is approximately 55 to 65% methane. The biogas composition is an essential parameter because it allows identifying the appropriate purification system, which aims to remove sulfuric gases and decrease the water volume, contributing to improve the combustion fuel conditions.

Currently, biogas production is mainly based on the anaerobic digestion of single energy crops. Maize, sunflower, grass, and Sudan grass are the most commonly used energy crops. In the future, biogas production from energy crops will increase and requires to be based on a wide range of energy crops that are grown in versatile, sustainable crop rotations.

A specific source of biogas is landfills. In a typical landfill, the continuous deposition of solid waste results in high densities and the organic content of the solid waste undergoes microbial decomposition. The production of methane rich landfill gas from landfill sites makes a significant contribution to atmospheric methane emissions. In many situations, the collection of landfill gas and production of electricity by converting this gas in gas engines is profitable and the application of such systems has become widespread. The benefits are obvious: useful energy carriers are produced from gas that would otherwise contribute to a buildup of methane in the atmosphere, which has stronger greenhouse gas impact than the carbon dioxide emitted from the power plant. This makes landfill gas utilization in general an attractive greenhouse gas mitigation option, which is being increasingly deployed in world regions.

In summary, biogas is most commonly produced by using animal manure mixed with water, which is stirred and warned inside an airtight container, known as a digester. The most important biogas components are methane, carbon dioxide, and sulfuric components. The gas generally composes of methane (55 to 65%), carbon dioxide (35 to 45%), nitrogen (0 to 3%), hydrogen (0 to 1%), and hydrogen sulfide (0 to 1%).

Anaerobic processes could either occur naturally or in a controlled environment such as a biogas plant. Organic waste such as livestock manure and various types of bacteria are put in an airtight container called digester so that the process could occur. In the complex process of anaerobic digestion, hydrolysis/acidification and methanogenesis are considered as rate-limiting steps.

Most biomass materials are easier to gasify than coal because they are more reactive with higher ignition stability. This characteristic also makes them easier to process thermochemically into higher-value fuels such as methanol or hydrogen. Ash content is typically lower than for most coals, and sulfur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest. A few biomass feedstocks stand out for their peculiar properties, such as high silicon or alkali metal contents – these may require special precautions for harvesting, processing, and combustion equipment. Note also that mineral content can vary as a function of soil type and the timing of feedstock harvest. In contrast to their fairly uniform physical properties, biomass fuels are rather heterogeneous with respect to their chemical elemental composition.

A number of processes allow biomass to be transformed into gaseous fuels such as methane or hydrogen. One pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Problems are intermittent production, low efficiency, and difficulty in constructing hydrogen collection and transport channels of low cost. A second pathway uses plant material such as agricultural residues in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment, but often with the energy produced only for onsite use, which often implies less than maximum energy yields. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. In addition to biogas, there is also the possibility of using the solid by-product as a biofuel.

The technologies for gas production from biomass include processes such as (i) fermentation, (ii) gasification, and (iii) direct biophotolysis.

See also: Gaseous Fuels.

Alternate Fuels – Liquid Fuels

Liquid fuels are combustible or energy-generating molecules that can be harnessed to create mechanical energy. It is the fumes of liquid fuels that are flammable instead of the fluid. Most liquid fuels in widespread use are derived from fossil fuel sources, but there are several types derived from non-fossil fuel sources – these are hydrogen, methanol ethanol, and biodiesel that are derived from non-fossil fuel sources which are also categorized as a liquid fuel.

Biofuel is a generic name for gaseous, liquid, or solid fuels that are not derived from fossil fuels or contain a proportion of non-fossil fuel. For the purposes of this text, the term alternate fuels is used to represent those fuels that are produced from plant sources as well as from other sources such as the organic constituents' (predominantly biological in nature) municipal and industrial waste. Thus, biofuels are *bio-materials* that are produced made from renewable biological sources which are now contemplated as grown specifically for the purpose of providing useful

heat upon combustion. Biofuels are produced from sources such as: corn, soybeans, flaxseed, rapeseed, sugarcane, palm oil, sugar beet raw sewage, food scraps, animal parts, and rice.

Biofuels are fuels derived from plant materials – are entering the market, driven by factors such as oil price spikes and the need for increased energy security. Examples of solid biofuels include wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops, and dried manure. Biofuels are also known as non-conventional fuels or alternative fuels. Alternative fuels can be classified as any fuel that is not derived from conventional sources like natural gas, crude oil, and coal.

See also: Liquid Fuels.

Alternate Fuels - Production

Biorenewable feedstocks can be converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or gaseous and liquid fuels. Main biomass conversion processes are – alphabetically rather than by preference – (i) anaerobic digestion, (ii) direct combustion, (iii) fermentation, (iv) gasification, and (v) pyrolysis. Each process has its own particular aspects, and process application is dependent upon the type of feedstock and the desired product(s).

The amount of hemicellulose and cellulose in wood and the chemical products desired determine the general type of process that might be used to hydrolyze wood. Hardwoods yield more five-carbon sugars than softwoods. Since, at this time, only the six-carbon sugars from cellulose are readily fermentable, softwoods are desired for ethanol production, but they are not as widely available as hardwoods. Hardwoods are more widely available now, so considerable effort has been expended to develop processes to utilize their unique constituents.

The main components of wood cells are cellulose (an insoluble substance which is the main constituent of plant cell walls and of vegetable fibers such as cotton. It is a polysaccharide consisting of chains of glucose monomers.), hemicellulose (a class of substances which occur as constituents of the cell walls of plants and are polysaccharides of simpler structure than cellulose.), and lignin (a complex organic polymer deposited in the cell walls of many plants, making them rigid and woody), forming some 99 % w/w of the wood material. Cellulose and hemicellulose are formed by long chains of carbohydrates, whereas lignin is a complicated component of polymeric phenolics. Lignin is rich in carbon and hydrogen, which are the main heat producing elements. Thus, the calorific value of lignin is higher than that of cellulose and hemicellulose (both are carbohydrate derivatives). Wood and bark also contain so-called extractives, such as terpenes, fats, and phenols. The amount of wood extractives is relatively small compared to the amount of extractives from bark and foliage.

The nitrogen (N) content of wood is approximately 0.75 %, varying somewhat from one tree species to another. For example, nitrogen-fixing alder (*Alnus* sp.) contains twice as much nitrogen as most coniferous trees. Wood has practically no sulfur (S) and, compared to many other fuels, the wood has a relatively low carbon content (some 50% of the dry weight) and high oxygen content (some 40% w/w), which leads to relatively low heating value per dry weight.

The collection of solid wastes is usually organized on a communal basis; in developing countries though, it may be organized (to a greater or lesser extent) on an informal basis. The treatment and disposal of solid wastes are definitely connected. Treatment is applied to recover useful substances or energy, to reduce waste volume, or to stabilize waste remains to be dumped or disposed of in landfills. Wastes may be treated before disposal to reduce the volume or to alter the characteristics of the waste which can be achieved by various physical, chemical, and biological processes, while combustion can be used to destroy some toxic organic chemicals. Where a method of waste disposal is not specified, the choice of disposal route will typically depend on (i) the availability of facilities, (ii) volume of waste material, and (iii) hydro-geological characteristics; the influence of industrial and environmental lobby groups must also be taken into account.

Provided that there is no shortage of land with suitable geological formations, landfill remains the principal final disposal route for the majority of wastes, even in highly industrialized countries. Where there is treatment, it is usually designed to reduce the volume of waste to be landfilled and includes compaction, shredding, baling, and combustion. Most solid wastes will therefore directly be disposed of in sanitary landfills.

The prefix *sanitary* is mainly to be understood as providing some protection for the population against airborne dust and litter, stench, rodents, and insects. Most of these nuisances can be prevented by the prompt covering of

freshly dumped waste with soil. However, to be able to call a waste tip or landfill *sanitary* from an environmental viewpoint requires more measures to be taken. The main environmental problem associated with landfilling is pollution of groundwater. Rainwater percolating through solid waste tends to carry large amounts of pollutants to groundwater aquifers if the underlying strata are pervious or fissured. Thus, wells drawing from the aquifers will be extracting groundwater contaminated by the leachate; such a situation is often difficult to remedy. Studies have shown that the leachate from solid wastes may have a pollution load up to 15 to 20 times higher than domestic wastewater.

Landfill tends to predominate as a waste disposal mode because it is regarded as an effective but low-cost method of disposal, also for hazardous waste. Even where other methods are more suitable for environmental reasons, the higher capital and (short-term) running costs mean that they cannot compete without government intervention. However, such cost calculations take no account of the longer term. In the long run, landfill of hazardous materials may impose a larger financial burden than other methods because of the high cost of ensuring that the site remains secure for the time it takes for the waste to be rendered harmless.

Alternate Fuels – Solid Fuels

Solid fuels are those fuels that are solid under ambient conditions and remain solid under mild heating. Thus, examples of solid fuels from biofuel feedstocks include wood and wood-derived charcoal and dried dung, particularly cow dung.

Compared to gaseous fuels and liquid fuels, solid fuels are often cheaper, easier to extract, more stable to transport, and in many places are more readily available. Coal, in particular, is utilized in the generation of electricity because it is less expensive and more powerful than its gaseous or liquid fuel counterparts. However, solid fuels are also heavier to transport, require more destructive methods to extract/burn, and often have higher carbon, nitrate, and sulphate emissions. With the exception of sustainable wood/biomass, solid fuel (such as peat or coal) is typically considered to be non-renewable because it requires thousands of years to form.

Alternative Energy

Alternative energy is a term for any nontraditional energy form, source, or technology differing from the current popular forms, sources, or technologies. Currently, the term alternative energy is generally used in the context of an alternative to energy deriving from the widely-used fossil fuels and thus includes energy derived from such environmentally preferred sources as biomass, geothermal, ocean, solar, tidal action, water power, wave action, and wind power. Many definitions of alternative energy use this term interchangeably with renewable energy.

The term alternative energy is also used for energy derived from sources and technologies that do not involve the depletion of natural resources (such as fossil fuel sources) or significant harm to the environment. As such, the term alternate energy is used synonymously with the terms renewable energy and green energy or green power. The three terms have also been delineated differently even though, by most definitions, there is substantial overlap between energy forms, sources, and technologies that fit into these three categories, and alternative energy often is applied to energy without undesirable environmental consequences or with lessened environmental impact. Renewable energy generally refers most specifically to energy derived from sustainable natural resources that are constantly replenished within a relatively short time frame (such as deriving from such renewable natural resources).

Amine Washing

Amine washing (more correctly olamine washing) of a gas stream involves the chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat, and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), di-isopropanolamine (DIPA), and diglycolamine (DGA) have

been used in commercial applications (Table A-19). Amine washing is the primary process for sweetening sour natural gas and is quite similar to the processes of glycol dehydration and removal of natural gas liquids by absorption.

The primary process for sweetening sour natural gas is quite similar to the processes of glycol dehydration and removal of natural gas liquids by absorption. In this case, however, amine (olamine) solutions are used to remove the hydrogen sulfide (the amine process).

Table A-19 Amines (olamines) used for gas processing.

Olamine	Formula
Ethanolamine (monoethanolamine) (MEA)	$\text{HOC}_2\text{H}_4\text{NH}_2$
Diethanolamine (DEA)	$(\text{HOC}_2\text{H}_4)_2\text{NH}$
Triethanolamine (TEA)	$(\text{HOC}_2\text{H}_4)_3\text{N}$
Diglycolamine (hydroxyethanolamine) (DGA)	$\text{H}(\text{OC}_2\text{H}_4)_2\text{NH}_2$
Diisopropanolamine (DIPA)	$(\text{HOC}_3\text{H}_7)_2\text{NH}$
Methyldiethanolamine (MDEA)	$(\text{HOC}_2\text{H}_4)_2\text{NCH}_3$

In the process, the sour gas is run through a tower, which contains the olamine solution. There are two principal amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. Like the process for the extraction of natural gas liquids and glycol dehydration, the amine solution used can be regenerated for reuse.

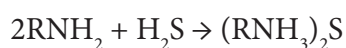
As currently practiced, acid gas removal processes involve the selective absorption of the contaminants into a liquid, such as an olamine (Table A-19), which is passed countercurrent to the gas. Then, the absorbent is stripped of the gas components (regeneration) and recycled to the absorber. The process design will vary and, in practice, may employ multiple absorption columns and multiple regeneration columns.

Liquid absorption processes (which usually employ temperatures below 50°C (120°F) are classified either as *physical solvent processes* or *chemical solvent processes*. The former processes employ an organic solvent, and absorption is enhanced by low temperatures, or high pressure, or both. Regeneration of the solvent is often accomplished readily. In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkaline solutions such as amines or carbonates. Regeneration (desorption) can be achieved by the use of reduced pressure and/or high temperature, whereby the acid gases are stripped from the solvent.

Regeneration of the solution leads to near complete desorption of carbon dioxide and hydrogen sulfide. A comparison between monoethanolamine, diethanolamine, and diisopropanolamine shows that monoethanolamine is the cheapest of the three but shows the highest heat of reaction and corrosion; the reverse is true for diisopropanolamine.

The processes using ethanolamine and potassium phosphate are now widely used. The ethanolamine process, known as the *Girbotol* process, removes acid gases (hydrogen sulfide, and carbon dioxide) from liquid hydrocarbons as well as from natural and from refinery gases. The Girbotol process uses an aqueous solution of ethanolamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

The chemistry can be represented by simple equations for low partial pressures of the acid gases:





At high acid gas partial pressure, the reactions will lead to the formation of other products:



The reaction is extremely fast, the absorption of hydrogen sulfide being limited only by mass transfer; this is not so for carbon dioxide.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Ammonia

Ammonia is a valuable chemical that is often produced from renewable sources (biomass) that contain nitrogen. It is recoverable from both the liquid and gas streams and can be readily separated from the liquid, by an ammonia still. The fixed salts must be treated with lime or caustic in a lime leg. The gaseous ammonia may be absorbed with sulfuric acid to produce ammonium sulfate, processed to anhydrous ammonia, or destroyed by combustion.

The standard procedure for the manufacture of ammonium sulfate from a gas stream involves several steps. The gas is first cooled to approximately 32°C (90°F) in an appropriate condensation system. Any tar, which is a very troublesome contaminant of ammonium sulfate (and vice versa), condenses and, in addition, much of the water containing approximately 25% of the ammonia (NH₃), primarily as ammonium (NH₄⁺) salts, also condenses. This water is rendered basic (lime treatment), thereby converting the ammonium ion to ammonia, which is recovered by being stripped off in a lime still and placed back in the coal gas stream. The coal gas stream is heated to above its dew point (approximately 65°C; 150°F), and the ammonia is adsorbed in 5 to 10% sulfuric acid solution contained in a lead-lined saturator at a temperature of 50 to 60°C (120 to 140°F); ammonium sulfate crystals precipitate from the sulfuric acid solution.

See also: Petrochemicals.

Anaerobic Digestion

Anaerobic digestion is the decomposition of biological wastes by microorganisms, usually under wet conditions, in the absence of air (oxygen), to produce a gas comprising mostly methane and carbon dioxide.

Anaerobic digestion of animal waste is the primary cause of odors, solids buildup and many diseases in swine, dairy, and poultry facilities, processing plants, municipal waste systems, and septic systems. Animal waste concentrated in pits under slatted floors or collected in holding tanks or lagoons has the natural tendency to involve an anaerobic process. Anaerobic digestion occurs when the anaerobic microbes are dominant over the aerobic microbes. Anaerobic microbes will naturally become dominant in pits or lagoons because of the lack of oxygen in solutions containing heavy concentrations of animal waste, which results in a high biological oxygen demand (BOD). These microbes feed on the animal waste at the bottom of the pits and lagoons. As they digest waste, large amounts of toxic gases are released due to the digestion processes common to the anaerobic microbes.

The anaerobic digestion of animal waste can be changed to aerobic digestion by proper applications of beneficial aerobic microbes in a highly concentrated form. If aerobic microbes are introduced into an environment that is lacking oxygen, they will begin to build oxygen into this environment as long as they survive and reproduce. Aerobes have the ability to do this in a liquid media or in the soil as long as there is an adequate moisture and food source for them to feed on and reproduce. The process is a multi-stage biological treatment process whereby bacteria, in the absence of oxygen, decompose organic matter to carbon dioxide, methane, and water (Table A-20).

Table A-20 Schematic of the anaerobic digestion process.

Feedstock	Products	Products	Products
Carbohydrates	Sugars	Carbon acids	Methane
Fats	Fatty acids	Alcohols	Carbon dioxide
Proteins	Amino acids	Hydrogen	
		Carbon dioxide	
		Ammonia	

In this way, the waste sludge is stabilized and the obnoxious odor is removed. The process can, however, be described adequately and simply as occurring in two stages, involving two different types of bacteria. The process occurs in the absence of air, the decomposition in this case is caused not by heat but by bacterial action. In the first stage, the organic material present in the feed sludge is converted into organic acids (also called volatile fatty acids) by acid forming bacteria. In the second stage, these organic acids serve as the substrate (food) for the strictly anaerobic methane-producing bacteria, which converts the acids into methane and carbon dioxide.

Any organic substance can become subject to anaerobic digestion so long as there are warm, wet, and airless conditions. For example, marsh gas is a product of the anaerobic digestion of vegetation at the bottom of ponds; this gas rises to the surface and bubbles, and the gas is also combustible. With the aid of human intervention, there are two products of this process, biogas and landfill gas. The chemical processes behind the production of these gases are complex. The end result of the process is a well-established sludge in which 40 to 60% of the volatile solids are destroyed. Finally, a combustible gas is produced consisting of 60 to 75% v/v methane and the remainder largely being carbon dioxide. (Table A-21).

Table A-21 Summary of most common chemical reactions in the anaerobic digestion process.

Substrate	Biochemical Reactions
Hydrogen and carbon dioxide	$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
Carbon monoxide	$4\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 3\text{CO}_2$
Alcohols	$4\text{CH}_3\text{OH} \rightarrow 3\text{CH}_4 + \text{CO}_2 + 2\text{H}_2\text{O}$ $\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ $4\text{HCOO}^- + 2\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
Monosaccharides	$\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{butyrate} + 2\text{HCO}_3^- + 3\text{H}^+$ $\text{C}_6\text{H}_{12}\text{O}_6 + 4\text{H}_2\text{O} \rightarrow 4\text{H}_2 + 2 \text{acetate} + 2\text{HCO}_3^- + 4\text{H}^+$
Organic Acids	$\text{Butyrate} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + 2 \text{acetate} + \text{H}^+$ $\text{Propionate} + 3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{acetate} + \text{HCO}_3^- + \text{H}^+$ $\text{HCOO}^- + 3\text{H}_2 + \text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{HCO}_3^-$ $4\text{CH}_2\text{NH}_2 + 2\text{H}_2\text{O} + 4\text{H}^+ \rightarrow 3\text{CH}_4 + \text{CO}_2 + 4\text{NH}_4^+$
Methanogenic substances	$2(\text{CH}_3)_2\text{NH} + 2\text{H}_2\text{O} + 2\text{H}^+ \rightarrow 3\text{CH}_4 + \text{CO}_2 + 2\text{NH}_4^+$ $4(\text{CH}_3)_3\text{N} + 6\text{H}_2\text{O} + 4\text{H}^+ \rightarrow 9\text{CH}_4 + 3\text{CO}_2 + 4\text{NH}_4^+$ $2\text{CH}_3\text{CH}_2\text{-N}(\text{CH}_3)_2 + 2\text{H}_2\text{O} \rightarrow 3\text{CH}_4 + \text{CO}_2 + 2\text{CH}_3\text{CH}_2\text{NH}_2$ $4\text{H}_2 + \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CH}_4 + 3\text{H}_2\text{O}$ $4\text{H}_2 + 2\text{HCO}_3^- + \text{H}^+ \rightarrow \text{acetate} + 4\text{H}_2\text{O}$
Sulfate	$4\text{H}_2 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + 3\text{H}_2\text{O} + \text{OH}^-$

Thus, simplified examples of the chemistry of anaerobic digestion process are as follows:

Carbohydrates $\rightarrow$ sugars $\rightarrow$ acids, alcohols $\rightarrow$ acetic acid, carbon dioxide, hydrogen

Fats → fatty acids → acids, alcohols → acetic acid, carbon dioxide, hydrogen

Protein → amino acids → ammonia, carbon dioxide, hydrogen

Organic acids formed in the first stage of the waste treatment process are converted to methane at the same rate at which they are formed. If not, they accumulate and ultimately lower the pH, leading to inhibition of the second stage of the digestion process and digester failure. Temperature must be maintained within certain ranges – heating increases the activity of the anaerobic bacteria, reducing the required digestion time. A pH of 7.0 to 7.5 is recommended to encourage the methane-producing stage.

The organic content of the sludge is significantly reduced by conversion into gaseous end-products; the obnoxious odor of the sludge is removed, and the final digested sludge has a characteristic tarry odor; fats and greases are broken down by the process. The liquid fraction (supernatant) contains increased levels of ammonia as a result of the breakdown of organic nitrogen (proteins). This makes the digested sludge liquor potentially suitable for agricultural use; the biogas that is formed is a mixture of carbon dioxide (CO₂) and methane (CH₄) that can be used for digester heating or to generate power.

The slow rate of bacterial growth usually requires long periods of time for start-up and limits the flexibility of the process to adjust to changing feed loads, temperatures, and other environmental conditions. In addition, the process is prone to upsets if not regularly monitored and if corrective action is not taken in time.

See also: Acetogenesis, Acidogenesis, Aerobic Digestion, Digester, Digestion, Hydrolysis, Methanogenesis.

Anaerobic Digestion – Gas Production

A typical gas system for the production of gas by anaerobic digestion comprises the digester cover, pressure and vacuum relief devices, water trap, flame trap, pressure regulator, gas meter, check valve, pressure gauges, waste gas burner, and a gas holder. The continuous stirred tank reactor (CSTR) is an example of a type of anaerobic digester.

The digester is covered to contain odors, maintain temperature, keep air out, and collect the gas. Fixed covers are more usual than floating covers. During normal operation, there is a space for gas collection between the cover and the liquid surface of the digester contents. The cover of a digester has certain unique features that the operating staff must be aware of, for example, how the variation in pressure and the level inside the digester may affect the cover. The biggest danger associated with the operation of fixed cover digesters occurs when the pressure relief device mounted on top of the digester fails or the sludge overflow line blocks and the liquid level in the digester continues to rise. In such a situation, the excess gas pressure inside the digester can exceed the maximum design pressure and damage the cover or its mountings. Fixed covers can also be damaged by excess negative pressure (vacuum) or if the rate of waste sludge withdrawal exceeds the feed rate or the vacuum relief device fails.

Gas leaving the digester is almost saturated with water vapor. As the gas cools, the water vapor condenses causing problems, which are more severe when digesters are heated. It is essential to remove as much of the moisture as possible before the gas comes into contact with the gas system devices. For this reason, water traps should be located as close to the digester as possible. All piping should be sloped a minimum of 1% toward the water trap, which should be situated at a low point in the gas line.

Flame traps are emergency devices installed in gas lines to prevent flames traveling back up the gas line (flash-back) and reaching the digester. The flame trap generally consists of a box filled with stone or a metal grid. If a flame develops in the gas line, the temperature of the flame is reduced below the ignition point as it passes through the trap and the flame is extinguished. Many anaerobic digestion waste treatment plants have a means of storing excess gas, either in the form of a floating roof on the digester or a separate gasholder.

A mixture of biogas and air can be explosive. Methane gas in concentrations of between 5% and 15% in air by volume is explosive and all piping and equipment must be sealed properly to prevent gas from escaping to the outside. In addition, all electrical installations, including light switches, and torches must be of the explosion-proof type, as the smallest spark could ignite escaped gases.

See also: Aerobic Digestion, Anaerobic Digestion.

Animal Waste

Animal wastes, or manure, as a source of biomass has the advantage that it is not competitive with other uses for this material. In the broader senses, animal waste can also include, in addition to animal manure, related animal waste (such as bedding and feed), dead animals, and waste from slaughter and meat processing. All such wastes generally fall in to a sub-class of biomass. Animal waste must of necessity come from confined operations such as dairy farms, cattle feedlots, and slaughter houses as well as meat processing plants.

Animal waste from farms and livestock/poultry and dairy production operations can severely threaten water quality if not managed properly and has the potential to contribute excess nutrients, pathogens, organic matter, solids, and odorous compounds to the environment. This pollution can cause eutrophication of surface waters, degradation of ground water quality, and threats to human health.

Historically, manure generated by livestock has been returned to the soil to improve its tilth and fertility. Recently, the use of animal waste to produce an renewable fuel (biogas) has become of interest. Anaerobic digestion is a renewable solution to livestock waste management that offers economic and environmental benefits.

Anaerobic digestion is a process to decompose organic material in the absence of oxygen. Biogas is produced as a waste product of digestion. In the first stage, the volatile solids in manure are converted into fatty acids by anaerobic bacteria (acid formers). In the second stage, these acids are further converted into biogas by more specialized bacteria (methane formers). With proper planning and design, this anaerobic-digestion process can be managed to convert the waste-stream from a farm into an asset and is, currently, the most appropriate option for farms and small-scale operation. The conversion of animal waste to gas by this process could result in animal husbandry operations being self-sufficient in energy.

Biogas produced in an anaerobic digester typically contains methane (60 to 70% v/v), carbon dioxide (30 to 40% v/v), various toxic gases (including hydrogen sulfide, ammonia, and sulfur-derived mercaptans), and 1 to 2% v/v water vapor.

See also: Agricultural Waste, Alternate Fuels, Anaerobic Digestion, Biogas.

Annual Removal

The annual removal is the net volume of growing stock trees removed from the inventory during a specified year by harvesting, cultural operations, such as, timber stand improvement, land clearing, and removal of trees killed or damaged by natural causes (natural losses), e.g. fire, wind blow, insects and diseases.

An example is clipping (i.e., harvesting aboveground plant biomass) which is common in agriculture and for bioenergy production.

Forest ecosystems contain large amounts of nutrients in woody biomass that may exist either as standing material, on the soil surface, or within the soil profile. Logs removed during timber harvesting remove considerable amounts of nutrients, and the disturbance caused by the process may sometime later, if not immediately, affect the amount of nutrients left on the site due to increased soil erosion, mineralization, and leaching. Thus, intensive harvesting, which removes a greater proportion of the forest biomass than conventional harvesting and the associated nutrients, may cause a decline in forest productivity.

Separately, warming and clipping alter soil and plant properties in either similar or contrasting fashions. For example, in grassland areas, both warming and clipping were observed to increase soil temperature and decrease soil moisture. In contrast, warming increased net primary productivity and plant carbon input to soil, but clipping reduced both. Moreover, warming led to an extended growing season length, while clipping caused compensatory root growth and stimulated exudation of carbon. The interactive effects of warming and clipping on these soil and plant properties rely on the mechanisms governing each single factor and the degree to which these factors interact. The responses of soil microbial communities to two or more factors are even less predictable than those of soil and plant properties, owing to their extremely high diversity.

See also: Biomass.

Apparent Density

The apparent density (*bulk density*) is the weight per unit volume of a material, such as coal, which includes the voids that exist in the tested material (Table A-22).

Table A-22 Measurement of the apparent density of materials.

Method	Use	Test
A	For fine granules and powders that can be poured through a small funnel.	Test is performed by pouring the material through a funnel into a cylinder of known volume. The apparent density is calculated by dividing the weight of the material in the cylinder by the volume of the cylinder.
B	For coarse, granular materials that either cannot be poured or that pour with difficulty through the funnel from Method A.	Test is performed by pouring the material through a funnel into a cylinder of known volume. The apparent density is calculated by dividing the weight of the material in the cylinder by the volume of the cylinder.
C	For coarse flakes, chips, cut fibers, or strands that cannot be tested with Methods A or B.	Test is performed by pouring the material into a graduated cylinder and allowing a 2300-g plunger to pack the material for 1 minute. The apparent density is taken as the mass of the material divided by the settled volume.

The bulk factor is the ratio of the density of a material after molding to the density of the raw material and provides a measure of the volume change that can be expected during processing.

The apparent density is not an intrinsic property of a material; it can change depending on how the material is handled. For example, a powder poured in to a cylinder will have a particular bulk density; if the cylinder is disturbed, the powder particles will move and usually settle closer together, resulting in a higher bulk density. For this reason, the bulk density of powders is usually reported both as “freely settled” and “tapped” density (where the tapped density refers to the bulk density of the powder after a specified compaction process, usually involving vibration of the container).

Aquaculture

Aquaculture is the raising of fish and other aquatic animals in a controlled environment – it is the farming of fish, shellfish, and other freshwater or marine (saltwater) creatures. Using geothermal water in aquaculture helps keep water temperatures consistent, which increases survival rates and makes the creatures grow faster. Low-temperature geothermal resources that are not hot enough to produce electricity are useful to fish farmers. Animals grown in water of the proper temperature grow faster and larger than those in cold water or water with fluctuating temperatures. They are also more resistant to disease and die less frequently.

Fish farmers with access to geothermal water can use it to regulate the temperatures of their fish ponds. Though the mechanism to accomplish this can be complicated, basically what happens is that the fish farmer opens valves to allow geothermal water to flow into the fish ponds until they reach the desired temperature. The valves are then closed to prevent the water from getting too hot. The mechanism is similar to adding hot water to a bathtub to bring the temperature to the desired level. Water flow can be adjusted throughout the year to account for air temperatures. Most ponds contain some mechanism to circulate the water and keep it all at an even temperature. Aquaculture operations usually have several ponds, which are kept small enough to be heated or cooled easily.

The main species of fish that are raised in geothermal waters are catfish, bass, trout, tilapia, sturgeon, giant freshwater prawns, alligators, snails, coral, and tropical fish. The warmth of geothermal water makes it possible to raise tropical marine (saltwater) species in cold, land-locked places such as Idaho.

Some creatures have a range of temperatures in which they thrive. For example, catfish and shrimp grow at approximately 50% of the optimum rate at temperatures between 20 and 26°C (68 and 79°F) and grow fastest at approximately 32°C (90°F), but they decline at temperatures higher than that. Trout thrive at around 15°C (60°F) but dislike lower or higher temperatures.

Like other direct uses of geothermal water, aquaculture allows an area to make use of groundwater that may not be hot enough to generate electricity, but is still hot enough to be useful as hot water. Arizona, for example, has a great deal of geothermal water that is under 150°C (300°F), which cannot generate electricity, but is very useful in aquaculture.

The fish grown in geothermal fisheries are healthier and stronger than fish grown in unheated fish ponds. Fish farmers can regulate temperature throughout the year to make sure the fish grow to a consistent size year-round. However, fish farmers must be careful to regulate water temperature. The water in and near the pipes bringing in the hot groundwater can get very hot, creating pockets that are too hot for fish. For aquaculture to work well, there must be a source of cool water in addition to the hot water. Some geothermal fisheries collect geothermal water in holding ponds and let it cool in order to regulate pond temperatures. If the water does not circulate evenly, there can also be cold spots. This can make the fish crowd into areas where the temperature is at the right level. The hot pipes also can be dangerous to human workers who must wade into the pools for repairs, feeding, and harvesting.

For the most part, using hot groundwater to heat fish ponds is good for the environment. A farm that uses geothermal water is not burning fossil fuels or other sources of heat to regulate water temperature and is therefore not emitting pollutants. Many geothermal aquaculture operations use water that has already been used by geothermal power plants or heating systems. The water has lost most of its heat but is still hot enough to raise the temperature of the fish ponds, so it can be put to a second use before disposal.

Aquaculture itself has both good and bad aspects for the environment. It takes pressure off wild fisheries, many of which have been severely overfished. In some areas, however, it contributes to pollution of the water.

Economically, using geothermal energy to heat water for aquaculture can have many benefits. Places that use water that has already been used for heating or electricity generation can heat their fish ponds essentially for no cost. They can also enjoy the economic benefit of selling the fish or prawns that they produce. Fish grown in geothermally heated water grow faster than fish in unheated water, so some fish farmers can grow extra fish crops for sale. Heated water makes it possible to grow fish in winter when it ordinarily would not be possible. Selling tropical fish for the pet store market can be quite profitable. Developing nations can export their fish produce for good prices, bringing foreign capital into the country.

See also: Aquasphere, Geothermal Energy.

Aquasphere

The Earth is a unique planet insofar as there is an abundance of water that is necessary to sustaining life on the Earth, and helps tie together the atmosphere, the land (the geosphere), and the oceans and rivers (the aquasphere) into an integrated system. Precipitation, evaporation, freezing and melting, and condensation are all part of the hydrological cycle, which is a never-ending global process of water circulation from clouds to land, to the ocean, and back to the clouds. This cycling of water is intimately linked with energy exchanges among the atmosphere, ocean, and land that determine the climate of the Earth and cause much of natural climate variability. The impacts of climate change and variability on the quality of human life occur primarily through changes in the water cycle.

The water systems of the Earth, often referred to as the aquasphere or the hydrosphere, refer to water in various forms: oceans, lakes, streams, snowpack, glaciers, the polar ice caps, and water under the ground (groundwater). An important aspect of the water systems is an aquifer which is a water-bearing (water-rich) subsurface formation (a subsurface zone) that yields water to wells. An aquifer may be porous rock, unconsolidated gravel, fractured rock, or

cavernous limestone. Aquifers are important reservoirs storing large amounts of water which, in theory, should be relatively free from evaporation loss or pollution. However, in practice, this is not always the case.

The aquasphere consists of a variety of non-oceanic water systems (Table A-23) that are essential to life, and all are interrelated, and the many interactions between the systems of the Earth are complex, and they are occurring constantly and simultaneously although the effects are not always obvious.

Table A-23 Sources of non-oceanic water and water systems.

Source	Description
Surface water	Water in a river, lake or fresh water wetland; the water is naturally replenished by precipitation and naturally lost through discharge to the oceans, evaporation, evapotranspiration, and groundwater recharge.
Groundwater	Fresh water located in the subsurface pore space of soil and rocks; also water that is flowing within aquifers below the water table.
Aquifer water	Fresh water in a layer of sediment or rock that is highly permeable; usually water in a layer of sand and gravel that have high permeability.
Unconfined aquifer	An aquifer that is overlaid by permeable earth materials and which is recharged by water seeping down from above in the form of rainfall and snow melt.
Confined aquifer	An aquifer which is sandwiched between two impermeable layers of rock or sediments and are recharged only in those areas where the aquifer intersects the land surface.

The oceans play a key role in the water cycle insofar as the oceans hold 97% v/v of the total water on the Earth and 78% v/v of the global precipitation occurs over the oceans, and it is the source of 86% v/v of global evaporation. Besides affecting the amount of atmospheric water vapor and hence rainfall, evaporation from the sea surface is important in the movement of heat in the climate system. Water evaporates from the surface of the ocean, mostly in warm, cloud-free subtropical seas. This continuing event cools the surface of the ocean, and the large amount of heat absorbed the ocean partially buffers the greenhouse effect from increasing carbon dioxide and other gases. Water vapor carried by the atmosphere condenses as clouds and falls as rain, mostly in the intertropical convergence zone (ITCZ), far from where it evaporated. Condensing water vapor releases latent heat which drives much of the atmospheric circulation in the tropics. This latent heat release is an important part of the heat balance of the Earth, and it couples the energy and water cycles of the Earth.

The intertropical convergence zone, known by sailors as the doldrums or the calms because of the monotonous, windless weather, is the area where the northeast and southeast trade winds converge. The zone encircles Earth near the thermal equator, although the specific position of the zone can vary on a seasonal basis. When the zone lies near to the geographic equator, it is referred to as the near-equatorial trough. When the intertropical convergence zone is drawn into and merges with a monsoonal circulation, the zone is sometimes referred to as a monsoon, a usage that is more common in Australia and parts of Asia.

The major physical components of the global water cycle include the evaporation from the ocean and land surfaces, the transport of water vapor by the atmosphere, precipitation onto the ocean and land surfaces, the net atmospheric transport of water from land areas to ocean, and the return flow of fresh water from the land back into the ocean. The additional components of oceanic water transport are few, including the mixing of fresh water through the oceanic boundary layer, transport by ocean currents, and sea ice processes.

On land, the situation is more complex, and includes the deposition of rain and snow on land; water flow in runoff; infiltration of water into the soil and groundwater; storage of water in soil, lakes and streams, and groundwater; polar and glacial ice; and use of water in vegetation and human activities. Processes labeled include precipitation, condensation, evaporation, evapotranspiration (from tree into atmosphere), radiative exchange, surface runoff, ground water and stream flow, infiltration, percolation, and soil moisture. Furthermore, in the water systems (particularly in the lakes) the term eutrophication becomes important. Eutrophication is the deterioration of the esthetic and lifesupporting qualities of lakes and estuaries, caused by excessive fertilization from effluents high in phosphorus, nitrogen, and organic growth substances. Algae and aquatic plants become excessive, and when they decompose, a sequence of objectional features arises.

Water for human consumption (and, in many cases as on farms for animal consumption) from such lakes must be filtered and treated. Diversions of sewage, better utilization of manure, erosion control, improved sewage treatment, and harvesting of the surplus aquatic crops alleviate the symptoms.

There are some extremely dramatic examples of Earth systems interacting, such as volcanic eruptions and ocean tsunamis, but there are also slow, nearly undetectable changes that alter ocean chemistry, the content of the atmosphere, and the microbial biodiversity in soil. Each part of the Earth, from inner core to the top of the atmosphere, has a role in making Earth suitable for the existence of billions of lifeforms ($1 \text{ billion} = 1 \times 10^9$). Within the aquasphere, the phenomenon known as (i) precipitation, (ii) evaporation, (iii) freezing, (iv) melting, and (v) condensation are part of the hydrological cycle – also known as the water cycle – which is a continuous global process of water circulation from clouds to land, to the ocean, and back to the clouds.

The water cycle describes the means by which water evaporates from the surface of the Earth, rises into the atmosphere, cools, condenses to form clouds, and falls again to the surface as precipitation. This system of the cycling of water is intimately linked with energy exchanges among the atmosphere, the ocean, and land that determine the climate of the Earth and cause much of natural climate variability. For example, approximately 75% of the energy (or heat) in the global atmosphere is transferred through the evaporation of water from the surface of the Earth. On land, water evaporates from the ground, mainly from soils, plants (through transpiration), lakes, and streams. In fact, approximately 15% v/v of the water entering the atmosphere is from evaporation from the land surfaces and evapotranspiration from plants which (i) cools the surface of the Earth, (ii) cools the lower atmosphere, and (iii) provides water to the atmosphere to form clouds.

The major physical components of the global water cycle include (i) the evaporation from the ocean and land surfaces, (ii) the transport of water vapor by the atmosphere and precipitation onto the ocean and land surfaces, (iii) the net atmospheric transport of water from land areas to ocean, and (iv) the return flow of fresh water from the land back into the ocean. The additional components of oceanic water transport are few, including the mixing of fresh water through the oceanic boundary layer, transport by ocean currents, and sea ice processes.

Water pollution has become a widespread phenomenon and has been known for centuries, particularly the pollution of rivers and groundwater. By way of example, in ancient time up to the early part of the 20th century, many cities deposited waste into the nearby river or even into the ocean. It is only very recently (because of serious concerns for the condition of the environment) that an understanding of the behavior and fate of chemicals, which are discharged to the aquatic environment as a result of these activities, is essential to the control of water pollution. In rivers, the basic physical movement of pollutant molecules is the result of advection, but superimposed upon this are the effects of dispersion and mixing with tributaries and other discharges. Some of the chemicals discharged are relatively inert, so their concentration changes only due to advection, dispersion, and mixing. However, many substances are not conservative in their behavior and undergo changes due to chemical or biochemical processes, such as oxidation.

In addition, there are many indications that the chemical materials in the aquasphere (also called, when referring to the sea, the marine aquasphere) are subject to intense chemical transformations and physical recycling processes imply that a total carbon approach is not sufficient to resolve the numerous processes occurring. The transport of anthropogenically produced or distributed compounds such as crude oil hydrocarbon derivatives and halogenated hydrocarbon derivatives, including the polychlorobiphenyl derivatives the DDT family, and the Freon derivatives and the chemistry of these chemicals in water is not fully understood.

The effects of a chemical released into the marine environment (or any part of the aquasphere) depends on several factors such as (i) the toxicity of the chemical, (ii) the quantity of the chemical, (iii) the resulting concentration of the chemical in the water column, (iv) the length of time that floral and faunal organisms are exposed to that concentration, and (v) the level of tolerance of the organisms, which varies greatly among different species and during the life cycle of the organism. Even if the concentration of the chemical is below what would be considered as the lethal concentration, a sub-lethal concentration of an chemical can still lead to a long-term impact within the aqueous marine environment. For example, chemically-induced stress can reduce the overall ability of an organism to reproduce, grow, feed, or otherwise function normally within a few generations. In addition, the characteristics of some chemicals can result in an accumulation of the chemical within an organism (*bio-accumulation*) and the organism may be particularly vulnerable to this problem. Furthermore, subsequent bio-magnification may also occur if the chemical (or a toxic product produced by one or more transformation reactions) can be passed on, following the food chain up to higher flora or fauna.

In terms of a chemical spill into the environment, the complex processes of transformation start developing almost as soon as the chemical contacts the land (or the water) although the progress, duration, and result of the transformations depend on the properties and composition of the chemical, parameters of the spill, and environmental conditions. The major operative processes are (i) physical transport, (ii) dissolution, (iii) emulsification, (iv) oxidation, (v) sedimentation, (vi) microbial degradation, (vii) aggregation, and (viii) self-purification.

In terms of *physical transport*, the distribution of oil spilled on the sea surface occurs under the influence of gravitational forces and is controlled by the viscosity of the (liquid) chemical as well as the surface tension of the water. In addition, during the first several days after a spill of a liquid chemical or a mixture of liquid chemicals, a part of spilled chemical may be lost through evaporation and any water-soluble constituents disappear into the water. The portion of the chemical mixture that remains is the more viscous fraction. Further changes take place under the combined impact of meteorological and hydrological factors.

Many organic chemicals are not *soluble* in water, although some constituents may be water-soluble to a certain degree, especially low-molecular-weight aliphatic and aromatic hydrocarbon derivatives. Polar compounds formed as a result of oxidation of some oil fractions in the marine environment also dissolve in seawater. Compared to evaporation process, the dissolution of organic chemicals in water is a slow process. However, the *emulsification* of a chemical (or chemicals) in the aquasphere does occur but depends predominantly on the presence of organic functional groups in the spilled material which can increase with time due to oxidation. The rate of emulsification process can be decreased by use of emulsifiers – surface-active chemicals with strong hydrophilic properties used to eliminate oil spills – which help to stabilize oil emulsions and promote dispersing oil to form microscopic (invisible) droplets that accelerates the decomposition of the chemicals in the water.

Oxidation is a complex process that can ultimately results in the destruction of the crude oil constituents. The final products of oxidation (such as hydroperoxide derivatives, phenol derivatives, carboxylic acid derivatives, ketone derivatives, and aldehyde derivatives) usually have increased water solubility. This can result in the apparent disappearance of the chemicals from the surface of the water. This is due to the incorporation of oxygen-containing functional groups into the chemicals which results in a change in density with an increase in the ability of the transformed chemicals to become miscible (or emulsify) and sink to various depths of the water system as these changes intensify. These chemical changes also result in an increase in the viscosity of the chemicals which promotes the formation of solid oil aggregates. The reactions of photo-oxidation, photolysis in particular, also initiates transformation of the more complex (polar) chemicals.

As these processes occur, some of the chemicals are adsorbed on any to suspended material and deposited on the floor of the water system (sedimentation), the rate of which is dependent upon the ocean depth – in deeper areas remote from the shore, sedimentation of oil (except for the heavy fractions) is a slow process. Simultaneously, the process of *biosedimentation* occurs – in this process, plankton and other organisms absorb the emulsified chemical – and the transformed chemical is sent to the bottom of the water system as sediment with the metabolites of the plankton and other organisms. However, this situation radically changes when the suspended chemical(s) oil reaches the bottom – the decomposition rate of the chemical ceases abruptly especially under the prevailing anaerobic conditions, and any chemicals that have accumulated inside the sediments can be preserved for many months and even years. These products can be swept to the edge of the water system (the river bank, the lake shore, or the beach in the case of a spill into an ocean) by turbulent condition at some later time.

Self-purification is a result of the processes previously described above in which a chemical in the environment rapidly loses the original properties and disintegrates into various products. These products may have different a chemical composition and structure to the original chemical and exist in different migrational forms, and they undergo chemical transformations that slow after reaching thermodynamic equilibrium with the environmental parameters. Eventually, the original and intermediate compounds disappear, and carbon dioxide and water form. This form of self-purification inevitably happens in water ecosystems if the amount of toxic chemicals spilled into the system does not exceed acceptable limits.

While acid-base reactions are not the only chemical reactions important in aquatic systems, they do present a valuable starting point for understanding the basic concepts of chemical equilibria in such systems. Carbon dioxide (CO_2), a gaseous inorganic chemical substance of vital importance to a variety of environmental processes, including growth and decomposition of biological systems, climate regulation, and mineral weathering, has acid-base properties that are critical to an understanding of its chemical behavior in the environment. The phenomenon of acid rain is another example of the importance of acid-base equilibria in natural aquatic systems.

Furthermore, the almost unique physical and chemical properties of water as a solvent are of fundamental concern to aquatic chemical processes. For example, in the liquid state, water has unusually high boiling point and melting point temperatures compared to its hydride analogues from the periodic table of the elements (Table 8.10) such as ammonia (NH_3), hydrogen fluoride (HF), and hydrogen sulfide (H_2S). Hydrogen bonding between water molecules means that there are strong intermolecular forces making it relatively difficult to melt or vaporize.

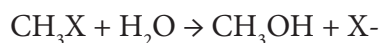
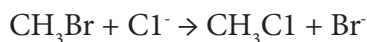
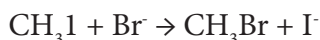
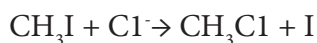
In addition, pure water has a maximum density at 4°C (39°F), higher in temperature than its freezing point (0°C , 32°F), and that ice is substantially less dense than liquid water, and is important (and fortunate) in several contexts. Thus, as water in a lake is cooled at its surface by loss of heat to the atmosphere, the ice structures formed will float. Furthermore, a dynamically stable water layer near 4°C (39°F), will tend to accumulate at the bottom of the lake, and the overlying, less dense water able to continue cooling down to the freezing point. This means that ice will eventually coalesce at the surface, forming an insulating layer that greatly reduces the rate of freezing of the underlying water. This situation is obviously important for plants and animals that inhabit lake waters.

In addition, the presence of salt components means that the temperature of maximum density for seawater is shifted to lower temperatures: in fact, the density of seawater continues to increase right down to the freezing point. The high concentration of electrolytes in seawater assist in breaking up the open, hydrogen-bonded ice-like structure of water near its freezing point. Because the salt components tend to be excluded from the ice formed by freezing seawater, sea ice is relatively fresh and still floats on water. Much of the salt it contains is not truly part of the ice structure but contained in brines that are physically entrained by small pockets and fissures in the ice.

The dielectric constant of water (78.2 at 25°C , 77°F) is high compared to most liquids. Of the common liquids, few have comparable values at this temperature, e.g., hydrogen cyanide (HCN, 106.8), hydrogen fluoride (HF, 83.6), and sulfuric acid (H_2SO_4 , 101). By contrast, most non-polar liquids have dielectric constants on the order of 2. The high dielectric constant helps liquid water to solvate ions, making it a good solvent for ionic substances, and arises because of the polar nature of the water molecule and the tetrahedrally-coordinated structure in the liquid phase.

In many electrolyte solutions of interest, the presence of ions can alter the nature of the water structure. Ions tend to orient water molecules that are near to them. For example, cations attract the negative oxygen end of the water dipole toward them. This reorientation tends to disrupt the ice-like structure further away. This can be seen by comparing the entropy change on transferring ions from the gas phase to water with a similar species that does not form ions.

As an example of chemical transformation that can occur in a water system, the chemistry of methyl iodide (which is thermodynamically unstable in seawater) is known and its chemical fate is kinetically controlled. The equations showing the fate of methyl iodide are as follows:



In this equation, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$

Chloride ion was theoretically predicted to be the most kinetically reactive species, with water second, and other anions of lesser importance. This suggested that methyl iodide in seawater would react predominantly via a nucleophilic substitution reaction with chloride ion to yield methyl chloride. Methyl iodide and the methyl chloride produced by would also react with water, although more slowly, to yield methanol and halide ions. According to these experiments, substantial amounts of methyl chloride should be formed in seawater. Methyl chloride has a long half-life for decomposition by known reactions in seawater. Hence, its presence could be a useful label for some surface-derived water masses. Methyl chloride is in fact found in the atmosphere, where compared to methyl iodide, it is less stable to photo-degradation reactions.

Steroids are a class of biogenic compounds which may serve as an indicator of certain processes transforming matter in seawater and sediments. The steroid hydrocarbon structure (Figure A-2) forms a relatively stable nucleus which may incorporate functional groups such as alcohols (sterol derivatives and stanol derivatives), ketone

derivatives (stanone derivatives) and olefin linkages (sterene derivatives) either in the four ring system or on the side chain originating at C-17.

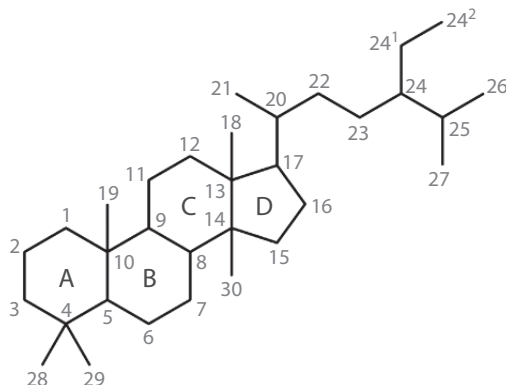


Figure A-2 The hydrocarbon framework of the steroid system (ring lettering and atom numbering are shown).

These compounds are produced by a wide variety of marine and terrestrial organisms and often have specific species sources. Diagenetic alteration of steroids by geochemical and biochemical processes can lead to the accumulation of transformed products in seawater and sediments.

Within the group of chlorinated compounds, chlorinated ethylene derivatives are the most often detected groundwater pollutants. Tetrachloroethylene (PCE) is the only chlorinated ethylene derivative that resists aerobic biodegradation. Trichloroethylene (TCE), all three isomers of dichloroethylene ($\text{CCl}_2=\text{CH}_2$ and the cis/trans isomers of $\text{CHCl}=\text{CHCl}$), and vinyl chloride ($\text{CH}_2=\text{CHCl}$) are mineralized in aerobic co-metabolic processes by methanotropic or phenol-oxidizing bacteria. Oxygenase derivatives with broad substrate spectra are responsible for the co-metabolic oxidation. Vinyl chloride is furthermore utilized by certain bacteria as carbon and electron source for growth. All chlorinated ethylene derivatives are reductively dechlorinated under anaerobic conditions with possibly ethylene or ethane as harmless end-products.

Tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) is dechlorinated to trichloroethylene ($\text{CCl}_2=\text{CHCl}$) in a co-metabolic process by methanogens, sulfate reducers, homoacetogen derivatives, and others. Furthermore, tetrachloroethylene and trichloroethylene serve in several bacteria as terminal electron acceptors in a respiration process. The majority of these isolates dechlorinate tetrachloroethylene and trichloroethylene to cis-1,2-dichloroethene, although they have been isolated from systems where complete dechlorination to ethene occurred.



1,1-Dichloroethylene



Cis-1,2-dichloroethylene



Trans-1,2-dichloroethylene

If chemicals have become subsurface contaminants that threaten important drinking water resources. A strategy to remediate such polluted subsurface environments is with the help of the degradative capacity of bacteria.

See also: Alicyclic Hydrocarbons, Alkaloids.

Aquatic Organisms

Aquatic organisms can be classified into each varying in the biological characteristics, habitat, and adaptations, but linked within a complex network of ecological roles and relationships.

Microorganisms (algae, bacteria, and fungi) are living catalysts that enable a vast number of chemical processes to occur in water and soil. The living organisms (biota) in an aquatic ecosystem may be classified as either autotrophic or heterotrophic. Autotrophic organisms utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. Algae are typical autotrophic aquatic organisms. Generally, carbon dioxide (CO_2), nitrate (NO_3), and phosphate derivatives (PO_4^{3-}) are sources of carbon, nitrogen, and phosphorus, respectively, for autotrophic organisms. Organisms that utilize solar energy to synthesize organic matter from inorganic materials are called producers.

Macrophytes are individual aquatic plants that can be seen by the unaided eye and can be categorized based on where and how they grow. **Rooted macrophytes** are rooted in the riverbed or lake substrate, and are thus restricted to areas where flow is low enough to permit fine sediments to accumulate. Rooted macrophytes may have leaves entirely submerged (under the water), floating on the surface, or emergent above the surface. In turbid water, little light penetrates and photosynthesis is restricted; hence, only plants with floating or emergent leaves can thrive. Rooted macrophytes may extract nutrients from the substrate as well as absorbing them from the water as algae do. Floating aquatic macrophytes are rootless plants that persist only in backwater areas where the flow slackens—otherwise, they are carried downstream. Because their photosynthetic surfaces are above the water surface, these plants can grow in deep, turbid water and places where rooting sites are sparse.

Macrophyte abundance can fluctuate seasonally as a result of scouring of the bottom sediments and washout of plants during heavy rains. For this reason, the number of macrophytes in river channels generally peaks during periods of low flow. Aquatic macrophytes are important in many aquatic systems, especially wetlands, slower moving water in streams and rivers, and in shallower areas of lakes. Aquatic macrophytes add three-dimensional complexity to aquatic habitat, and can provide habitat, refuge, and spawning areas for animals such as aquatic insects and fish, as well as a surface for periphyton growth. As they are primary producers, aquatic macrophytes produce organic matter which can be eaten by some fish; however, most of this plant material is unpalatable to herbivores while it is alive.

Large populations of aquatic macrophytes can have negative effects on aquatic ecosystems and the people that rely on them. In some cases, floating plants are so numerous that they form dense mats covering the water surface. Their buoyant leaf crowns merge above the surface, while the root masses dangle below into the water. The interlocking vegetation mat blocks light penetration down the water column and prevents the growth of other plants. In extreme cases, the underlying water becomes deoxygenated, and floating plants turn into a nuisance by inhibiting the passage of boats and interfering with fishing. Invasive species of macrophytes can be particularly disruptive to natural aquatic ecosystems.

Invertebrates include all animals without a backbone. Invertebrates are far more diverse and abundant than vertebrates, and many groups of invertebrates are found in aquatic systems. Invertebrates living on or in aquatic sediments are termed benthic invertebrates. Benthic invertebrate communities – including measurements of population abundance and diversity – are often used as indicators of aquatic ecosystem health.

Zooplankton are aquatic animals that cannot swim against water currents, typically because they are too small to do so. However, many zooplankton can swim significant distances in fairly still waters. Because they cannot swim against currents, zooplankton are more important in lakes than in running water, as running water usually carries them downstream faster than they can reproduce. However, they can be abundant in large slow flowing rivers. Zooplankton are heterotrophic and are significant sources of energy and nutrients to carnivorous invertebrates and some vertebrates.

Heterotrophic organisms utilize the organic substances produced by autotrophic organisms as energy sources and as the raw materials for the synthesis of their own biomass. Decomposers (or reducers) are a subclass of the heterotrophic organisms and consist of chiefly bacteria and fungi, which ultimately break down material of biological origin to the simple compounds originally fixed by the autotrophic organisms.

Insects are the most diverse group of animals on earth – most insects are terrestrial, while some have life stages that are aquatic (such as dragonflies and mosquitoes). Some insects are entirely aquatic (such as the aquatic beetles). While most aquatic insects live on or near the bottom of waterbodies, though some can swim into the water column. Most aquatic insects have gills and need water with dissolved oxygen, while others, such as mosquito larvae, breathe

through the surface film of still waters. Stream and river insects are crucial in the processing of organic matter. Some scrape biofilm; others shred larger leaves into smaller particles, while still others filter or collect these smaller particles. This chain of processing reduces large organic matter to successively smaller and smaller particles.

Fish display every major feeding type: (i) herbivorous fish feed on periphyton or macrophytes, or may even filter phytoplankton from the water, (ii) carnivorous fish feed on mollusks, worms, insects, zooplankton, and other fish, (iii) omnivorous fish may feed on specific types of prey, or feed indiscriminately on nearly anything they can consume. Due to this diversity in modes of feeding, different fish can occupy different places in a food chain.

As with feeding behavior, some fish occupy specific habitats, while others can be found in a wide variety of lakes and rivers. The distribution of fish can be influenced by a large number of factors, including (i) oxygen concentration, (ii) temperature, (iii) the presence of macrophytes, (iv) the availability of suitable substrate for spawning, and (v) current speed in streams and rivers. Changes in fish habitat (such as reduction of flooding due to damming) can favor some types of fish, and disadvantage others.

See also: Aquasphere.

Aquatic Plants

Aquatic plants (also known as hydrophytic plants, hydrophytes) are plants that have adapted to living in aquatic environments and are also referred to as hydrophytes or macrophytes to distinguish them from algae and other microphytes. A macrophyte is a plant that grows in or near water and is emergent, submergent, or floating. The three types of aquatic plants are (i) submerged aquatic weeds, submerged plants are rooted in the pond bottom and grow up through the water column, (ii) emergent aquatic weeds, and (iii) free floating aquatic weeds.

Aquatic plants include kelp from the ocean, and freshwater plants such as algae, water hyacinth, and duckweed. Aquatic plants are considered to be a sub-category of biomass and the plants, like wood products, dried vegetation, and crop residues, have the potential to produce biomass fuels.

Aquatic plants have adapted to living in or on aquatic environments and, because living on or under water surface requires numerous special adaptations, aquatic plants can only grow in water or permanently saturated soil. As opposed to typical plant types, aquatic plants do not have a problem in retaining water due to the abundance of water in its environment. This means that the plant has less need to regulate transpiration which requires less energy and increases the possible benefits.

Enhancing the growth rate of these plants by increased nutrient supply, for example, from carbon dioxide in flue gases, or growing suitable plants in conjunction with municipal wastewater treatment facilities, has received some attention. While quantitative data and costs for this resource are limited, full development of the aquatic biomass energy potential is not expected to approach 1% of total US energy requirements.

Algae are tiny aquatic plants have the potential to grow extremely fast in the hot, shallow, saline water found in some lakes in the desert Southwestern United States. Forms of algae thrive on carbon dioxide, and emissions from power plants have been used to feed the plants, which are then used in biofuels.

See also: Algae, Aquasphere, Biomass.

Aquiclude, Aquitard, Aquifuge

An aquiclude is a water-bearing layer in which both the horizontal and vertical flow components are so small that they can be neglected. The groundwater flow in an aquiclude is assumed to be zero.

Impervious rock in the unsaturated zone may retain water infiltrating from the surface to produce a perched water table that is above the main water table and from which water may be extracted. However, the amounts of water that can be extracted from such a formation are limited and the water is vulnerable to contamination.

An aquitard is a water-bearing layer in which the horizontal flow component is so small with respect to the vertical flow component that it can be neglected. The groundwater flow in an aquitard is assumed to be predominantly vertical. An aquifuge is a geological formation with low permeability and porosity. This does not transmit any groundwater and does not contain groundwater in appreciable quantities.

See also: Aquifer, Geohydrology, Groundwater Aquifer.

Aquifer

An aquifer is a water-bearing subsurface zone in which the vertical flow component is so small with respect to the horizontal flow component that it can be neglected.

The groundwater flow in an aquifer is assumed to be predominantly horizontal. The term aquifer is synonymous with water-bearing formation. An aquifer may be porous rock, unconsolidated gravel, fractured rock, or cavernous limestone. Economically important amounts of water may vary from less than a gallon per minute for cattle water in the desert to thousands of gallons per minute for industrial, irrigation, or municipal use.

Aquifers are important reservoirs storing large amounts of water relatively free from evaporation loss or pollution. If the annual withdrawal from an aquifer regularly exceeds the replenishment from rainfall or seepage from streams, the water stored in the aquifer will be depleted. Lowering the pressure in an aquifer by overpumping may cause the aquifer and confining layers of silt or clay to be compressed under the weight of the overburden. The resulting subsidence of the ground surface may cause structural damage to the aquifer and to surface buildings, damage to wells, and other problems.

Depending on the permeability of the layers bordering the aquifer, a distinction is made between: (i) a confined aquifer, (ii) a semi-confined aquifer, (iii) an unconfined aquifer, and (iv) a semi-unconfined aquifer.

A confined aquifer is an aquifer in which groundwater is held under pressures greater than atmospheric pressure by upper and lower confining layers, forcing water to rise in wells to heights above the top of the aquifer (artesian wells; also known as an artesian aquifer). The confined aquifer is typically sandwiched between two impermeable layers of rock or sediments and are recharged only in those areas where the aquifer intersects the land surface. The pressure of the water in confined aquifers is higher than atmospheric pressure, which is why when a well is bored into the aquifer, the water rises up the well tube, to a level higher than the aquifer.

If the water level in an artesian well stands above the land surface, the well is a flowing artesian well. A particular aquifer at one place may be a confined aquifer but in other places may behave as an un-confined aquifer, when the water level falls below the base of the overlying confining layer. In the igneous and metamorphic rocks, groundwater may occur in confined conditions in joints and fractures. In volcanic rocks, the interflow spaces and the vesicular beds form confined aquifers. Examples of flowing artesian wells are found in the hard rock areas of South India.

A semi-confined aquifer is an aquifer that is situated between confining layers with a lower permeability. The upper (and lower) confining layers are semi-pervious, through which vertical leakage takes place due to head difference. These transmit limited quantities of groundwater. The general direction of flow in a semi-confined aquifer is horizontal. The preferred direction of flow in the confining layers above and below is vertical.

An unconfined aquifer is not overlain by any confining layer, but it has a confining layer at its bottom and is recharged by water seeping down from above in the form of rainfall and snow melt. Thus, an unconfined aquifer is a partly saturated aquifer bounded below by an aquiclude and above by the free water table or phreatic surface. At the free water table, the groundwater is at atmospheric pressure. In general, the water level in a well penetrating an unconfined aquifer does not rise above the water table, except when there is vertical flow. The unconfined aquifer is normally partly saturated with water, and the top of the saturated surface is known as the water table, which is under atmospheric pressure – it is also known as a water table/phreatic aquifer. The water level in wells penetrating this aquifer indicates the position of the water table in the surrounding aquifer.

A semi-unconfined aquifer (also known as leaky aquifer) is an aquifer which exhibits characters in between semi-confined and unconfined aquifers as the permeability of the fine grained overlying layers is more than in a semiconfined aquifer and the horizontal flow component in it cannot be neglected. This type of aquifer is a completely saturated aquifer that is bounded below by an aquiclude and above by an aquitard.

If the overlying aquitard extends to the land surface, the aquifer may be partly saturated, but if the aquifer is overlain by an unconfined aquifer that is bounded above by the water table, the aquifer will be fully saturated. If there is hydrological equilibrium, the piezometric level in a well tapping a leaky aquifer may coincide with the water table. In areas with upward or downward flow (i.e., in discharge or recharge areas) the piezometric level may rise above or fall below the water table.

Finally, a multi-layered aquifer is a succession of leaky aquifers sandwiched between aquitards. Systems of inter-bedded permeable and less permeable layers are common in deep sedimentary basins.

See also: Aquiclude, Aquitard, Aquifuge.

Aromatic Hydrocarbons

An aromatic hydrocarbon (sometimes referred to as an arene) is a hydrocarbon of which the molecular structure incorporates one or more planar sets of six carbon atoms that are connected by delocalized electrons numbering the same as if they consisted of alternating single and double covalent. Aromatic hydrocarbons contain carbon and hydrogen atoms only.

Benzene (C_6H_6) is the least complex aromatic hydrocarbon, and it was the first one named as such. Each carbon atom in the hexagonal cycle has four electrons to share. One goes to the hydrogen atom, and one to each of the two neighboring carbon atoms which leaves one electron to share with one of the two neighboring carbon atoms, thus creating a double bond with one carbon and leaving a single bond with the other, which is why some representations of the benzene molecule portray it as a hexagon with alternating single and double bonds.

After benzene, aromatic hydrocarbons can be polycyclic (also called condensed aromatic systems) (Figure A-3):

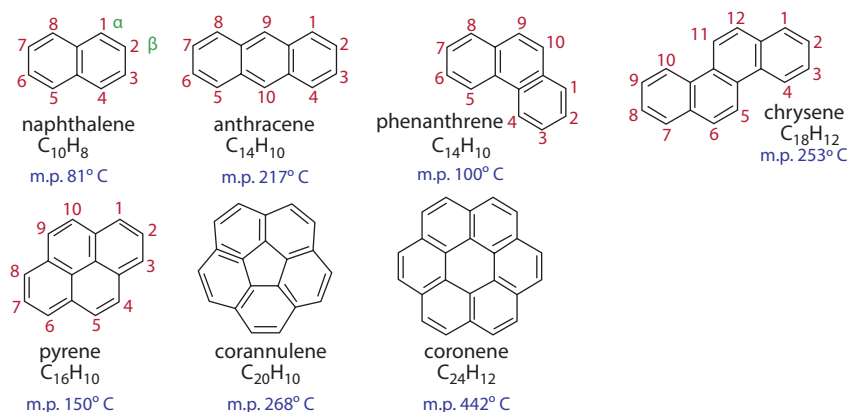


Figure A-3 Examples of aromatic hydrocarbons showing the alternating double bonds and single bonds.

Other depictions of the structure portray the hexagon with a circle inside it, to indicate that the six electrons are floating around in delocalized molecular orbitals the size of the ring itself. This represents the equivalent nature of the six carbon-carbon bonds all of bond order 1.5; the equivalency is explained by resonance forms. The electrons are visualized as floating above and below the ring, with the electromagnetic fields they generate acting to keep the ring flat.

The general properties of aromatic hydrocarbons are: (i) they display aromaticity, (ii) the carbon-hydrogen ratio is high, (iii) they burn with a strong sooty yellow flame because of the high carbon-hydrogen ratio, and (iv) they undergo electrophilic substitution reactions and nucleophilic substitution reaction.

See also: Alkenes, Alicyclic Hydrocarbons, Aliphatic Hydrocarbons.

Arsenic and Selenium

Arsenic is a notoriously poisonous metalloid with many allotropic forms, including a yellow (molecular non-metallic) and several black and gray forms (metalloids). Three metalloid forms of arsenic, each with a different crystal structure, are found free in nature. However, it is more commonly found as arsenide and in arsenate compounds, several hundreds of which are known. Arsenic and its compounds are used as pesticides, herbicides, insecticides, and in various alloys.

Selenium a nonmetal, chemically related to sulfur and tellurium, which rarely occurs in its elemental state in nature. Isolated selenium occurs in several different forms, the most stable of which is a dense purplish-gray semi-metal (semiconductor) form that is structurally a trigonal polymer chain. It conducts electricity and is used in photocells. Selenium is found in economic quantities in sulfide ores such as pyrite FeS_2 , partially replacing the sulfur in the ore matrix. Minerals that are selenide or selenate compounds are also known, but all are rare.

Selenium salts are toxic in large amounts, but trace amounts of the element are necessary for cellular function in most, if not all, animals, forming the active center of the enzymes glutathione peroxidase and thioredoxin reductase (which indirectly reduce certain oxidized molecules in animals and some plants) and three known deiodinase enzymes (which convert one thyroid hormone to another).

Arsenic and selenium occur in biomass to the extent of several parts per million and, on combustion of the coal, a varying quantity of these elements are released or retained in the ash, depending largely on the conditions under which the combustion takes place and on the nature of the ash.

Arsenic and selenium are determined by mixing a weighed sample with the Eschka mixture followed by ignition 750°C (1,380°F). The mixture is dissolved in hydrochloric acid, and the gaseous hydride of each element is generated from the appropriate oxidation state and determined by atomic absorption spectrophotometry. The method permits measurement of the total arsenic and selenium content of coal for the purpose of evaluating these elements where they can be of concern, for example, in coal combustion. When coal samples are prepared for analysis in accordance with standard procedure, the arsenic and selenium are quantitatively retained and are representative of the total amounts in the coal

See also: Periodic Table of the Elements.

Asabe Standard X593

The American Society of Agricultural and Biological Engineers (ASABE) is an educational and scientific organization dedicated to the advancement of engineering applicable to agricultural, food, and biological systems. Founded in 1907 and headquartered in St Joseph, Michigan, ASABE comprises 9,000 members in more than 100 countries. ASABE membership is open to all (engineers as well as non-engineers) who are interested in the knowledge and application of engineering in agricultural, food, and biological systems.

ASABE Standard X593 is the standard introduced by the American Society of Agricultural and Biological Engineers (ASABE) entitled "Terminology and Definitions for Biomass Production, Harvesting and Collection, Storage, Processing, Conversion and Utilization."

The purpose of the standard is to provide uniform terminology and definitions in the general area of biomass production and utilization. This standard includes many terminologies that are used in biomass feedstock production, harvesting, collecting, handling, storage, pre-processing and conversion, bioenergy, biopower, and bioproducts. The terminologies were reviewed by many experts from all of the different fields of biomass and bioenergy before being accepted as part of the standard.

See also: Biomass.

Ash

Ash is the noncombustible residue remaining after complete combustion of a fuel and is composed primarily of oxides and sulfates, and it should not be confused with mineral matter, which is composed of the unaltered inorganic minerals in the fuel. In very general terms, the inorganic materials in most solid fuels, including biomass, can be divided into two broad fractions: (i) inherent inorganic material and (ii) extraneous inorganic material.

The inherent inorganic material exists as part of the organic structure of the fuel, and is most commonly associated with the oxygen-, sulfur-, and nitrogen-containing functional groups. These organic functional groups can provide suitable sites for the inorganic species to be associated chemically in the form of cations or chelates. Biomass materials tend to be relatively rich in oxygen-containing functional groups, and a significant fraction of the inorganic material in some of the lower ash biomass fuels is commonly in this form. It is also possible for inorganic species to be present in fine particulate form within the organic structure of some of the fuels, and to behave essentially as an inherent component of the fuel.

The extraneous inorganic material has been added to the fuel through geological processes, or during harvesting, handling, and processing of the fuel. Biomass fuels, for instance, are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling and storage.

Ash is quantitatively and qualitatively different from the mineral matter originally present in the fuel because of the various changes that occur, such as loss of water from silicate minerals, loss of carbon dioxide from carbonate minerals, oxidation of iron pyrite to iron oxide, and fixation of oxides of sulfur by bases such as calcium and magnesium. In fact, incineration conditions determine the extent to which the weight changes take place and it is essential that standardized procedures be closely followed to ensure reproducibility.

Thus, ash is formed as the result of chemical changes that take place in the mineral matter during the *ashing* process. The quantity of ash can be more than, equal to, or less than the quantity of mineral matter in the fuel, depending on the nature of the mineral matter and the chemical changes that take place in ashing. The various changes that occur include (i) loss of water from silicate minerals, (ii) loss of carbon dioxide from carbonate minerals, (iii) oxidation of iron pyrite to iron oxide, and (iv) fixation of oxides of sulfur by bases such as calcium and magnesium. In fact, incineration conditions determine the extent to which the weight changes take place and it is essential that standardized procedures be closely followed to ensure reproducibility.

The use of fuel with mineral matter that gives a high alkali oxide ash often results in the occurrence of slagging and fouling problems, especially in gasifiers. As oxides, most ash elements have high melting points, but they tend to form complex compounds (often called eutectic mixtures) that have relatively low melting points. On the other hand, high-calcium-low-iron ash coals tend to exhibit a tendency to produce low-melting range slag, especially if the sodium content of the slag exceeds approximately 4% w/w.

The chemical composition of the ash is an important factor in fouling and slagging problems and in the viscosity of ash in wet bottom and cyclone furnaces. The potential for the mineral constituents to react with each other as well as undergo significant mineralogical changes is high. In addition, fuel with a high iron content (usually >20% w/w ferric oxide) ash typically exhibits ash-softening temperatures under 1,205°C (2,200°F). Also, volatile alkali compounds lower the fusion temperature of ash. In conventional combustion equipment having furnace gas exit temperatures above 790°C (1,450°F, combustion of agricultural residue causes slagging and deposits on heat transfer surfaces. Specially designed boilers with lower furnace exit temperatures could reduce slagging and fouling from combustion of these fuels. Low-temperature gasification may be another method of using these fuels for efficient energy production while avoiding the slagging and fouling problems encountered in direct combustion.

In some test methods, it is recommended that the color of the ash should be noted as it gives an approximate indication of the fusion point. Generally, highly colored ash has a low fusion point while white ash, provided they are relatively no basic oxides, has a high fusion point.

See also: Biomass Ash, Bottom Ash, Fly Ash.

Ash Analysis

Ash analyses are used for evaluation of the corrosion, slagging, and fouling potential of ash. Typically, the ash constituents of interest are silica (SiO_2), alumina (Al_2O_3), titania (TiO_2), ferric oxide (Fe_2O_3), lime (CaO), magnesia (MgO), potassium oxide (K_2O), sodium oxide (Na_2O), and sulfur trioxide (SO_3). An indication of ash behavior can be estimated from the relative percentages of each constituent.

The determination of mineral ash in a fuel is usually by heating (burning) an accurately-weighed sample of the coal in an adequately ventilated muffle furnace at temperatures in the range 700 to 750°C (1,290 to 1,380°F) for 4 hours. Typically, the experimental data should be reproducible within $\pm 0.2\%$ of the end result. Other standard test methods may vary and require somewhat higher temperatures for the determination of the ash in coal.

See also: Ash, Ash Content.

Ash Composition

The chemical composition of ash is an important factor in fouling and slagging problems and in the viscosity of ash in wet bottom and cyclone furnaces. The potential for the mineral constituents to react with each other as well as undergo significant mineralogical changes is high. The use of biomass feedstocks with mineral matter that gives a high alkali oxide ash often results in the occurrence of slagging and fouling problems. As oxides, most ash elements have high melting points, but they tend to form complex compounds (often called eutectic mixtures) which have relatively low melting points. On the other hand, high-calcium-low-iron ash coals exhibit a tendency to produce low-melting range slags, especially if the sodium content of the slag exceeds approximately 4% w/w.

One form of ash is fly ash, one of the residues generated during combustion. Fly ash is generally captured from the chimneys of power plants, and is one of two types of ash that are jointly known as ash; the other form of coal ash is bottom ash, which is removed from the bottom of coal furnaces.

Depending upon the source and makeup of the feedstock to the combustor, the components of fly ash vary considerably (Table A-24), but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO), both being endemic ingredients in many coal bearing rock strata.

Table A-24 Common constituents of fly ash (% w/w).

Coal:	Bituminous	Subbituminous	Lignite
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	20-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40

Toxic constituents depend upon the specific coal bed makeup, but may include one or more of the following elements or substances (in alphabetical order and not in order of occurrence) in quantities from trace amounts to several percent: arsenic, beryllium, boron, cadmium, chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium. Organic constituents of ash include dioxins and polynuclear aromatic compounds.

Fly ash solidifies while suspended in the exhaust gases and is collected by electrostatic precipitators or filter bags (Baghouse). Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape and range in size from 0.5 micron to 100 μm . They consist mostly of silica (SiO_2), which is present in two forms: amorphous (rounded and smooth) and crystalline (sharp, pointed, and hazardous), aluminum oxide (Al_2O_3), and iron oxide (ferric oxide, Fe_2O_3). Fly ash is generally highly heterogeneous and consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), and various iron oxides.

In the past, fly ash was generally released into the atmosphere, but pollution control equipment mandated in recent decades now requires that it be captured prior to release. In the United States, fly ash is generally stored or placed in landfills or is often used to supplement Portland cement in concrete production as well as in the synthesis of geopolymers and zeolites.

Ash Content

Ash content (which is a thermal manifestation of the inorganic content of a fuel, such as biomass) is the inorganic oxides that remain after complete combustion of the feedstock. The amount of ash between different types of feedstocks differs widely (0.1% w/w for wood and up to 15% w/w for some agricultural products) and influences the use of the fuel as well as the design of the reactor, particularly the ash removal system. The chemical composition of the ash is also important because it affects the melting behavior of the ash. Ash melting can cause slagging and channel formation in the reactor. Slag can ultimately block the entire reactor.

Generally, the ash-forming inorganic materials in most solid fuels, including biomass, can be divided into two broad fractions: (i) the inherent inorganic material and (ii) the extraneous inorganic material.

The inherent inorganic material exists as part of the organic structure of the fuel, and is most commonly associated with the oxygen-, sulfur-, and nitrogen-containing functional groups. These organic functional groups can provide suitable sites for the inorganic species to be associated chemically in the form of cations or chelates. Biomass materials tend to be relatively rich in oxygen-containing functional groups, and a significant fraction of the inorganic material in some of the lower ash biomass fuels is commonly in this form. It is also possible for inorganic species to be present in fine particulate form within the organic structure of some of the fuels, and to behave essentially as an inherent component of the fuel.

The extraneous inorganic material has been added to the fuel through geological processes, or during harvesting, handling, and processing of the fuel. Biomass fuels, for instance, are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling, and storage.

The most commonly applied technique for the determination of the ash content and ash composition of coals and other solid fuels in the laboratory involves heating the fuel slowly in air to constant mass at a temperature of 815°C (1,500°F), and subjecting the resultant ash residue to chemical elemental analysis. The ash residue is normally weighed to provide an estimate of the ash content of the fuel, and then analyzed for the 10 major elements present in coal ashes, i.e., Si, Al, Fe, Ca, Mg, Ti, Na, K, P, and S. The elemental concentrations are conventionally expressed as oxides, in their highest oxidation states. The analysis of the laboratory-prepared ash for its trace element content is also fairly common practice. This is a perfectly reasonable and practical approach for most coals, and many other solid fuels, and has been applied for biomass ash analysis.

Biomass feedstocks and fuels exhibit a wide range of physical and chemical properties (Table A-25), but despite the wide range of possible sources, biomass feedstocks are remarkably uniform in many of their fuel properties, compared with competing feedstocks such as coal or crude oil. For example, there are many types of coal whose gross heating value ranges from 8,600 to 12,900 Btu/lb). However, nearly all kinds of biomass feedstocks destined for combustion fall in the range 6,450 to 8,200 Btu/lb). For most agricultural residues, the heating values are even more uniform – approximately 6,450 to 7,300 Btu/lb. The values for most woody materials fall into the range 7,750 to 8,200 Btu/lb.

Table A-25 Properties of biomass and other fuel sources.

		Chemical Characteristics			
		Ash, %	Sulfur, % w/w	Potassium, % w/w	Ash melting temperature (°C)
Bioenergy Feedstocks	corn stover	5.6			
	sweet sorghum	5.5			
	sugarcane bagasse	3.2-5.5	0.10-0.15	0.73-0.97	
	sugarcane leaves	7.7			
	hardwood	0.45	0.009	0.04	
	softwood	0.3	0.01		
	hybrid poplar	0.5-1.5	0.03	0.3	1,350
	bamboo	0.8-2.5	0.03-0.05	0.15-0.50	
	switch grass	4.5-5.8	0.12		1,016
	Miscanthus	1.5-4.5	0.1	0.37-1.12	1,090
	Arundo donax	5-6	0.07		
Liquid Biofuels	bioethanol		<0.01		N/A
	biodiesel	<0.02	<0.05	<0.0001	N/A
Fossil Fuels	Coal (low rank; lignite/sub-bituminous)	5-20	1.0-3.0	0.02-0.3	Approximately 1,300
	Coal (high rank; bituminous/anthracite)	1-10	0.5-1.5	0.06-0.15	Approximately 1,300
	Oil (typical distillate)	0.5-1.5	0.2-1.2		N/A

The most commonly applied technique for the determination of the ash content and ash composition of coals and other solid fuels in the laboratory involves heating the fuel slowly in air to constant mass at a temperature of

815°C (1,500°C), and subjecting the resultant ash residue to chemical elemental analysis. The ash residue is normally weighed to provide an estimate of the ash content of the fuel, and then analyzed for the 10 major elements present in coal ashes, i.e., Si, Al, Fe, Ca, Mg, Ti, Na, K, P, and S. The elemental concentrations are conventionally expressed as oxides, in their highest oxidation states. The analysis of the laboratory-prepared ash for its trace element content is also fairly common practice. This is a perfectly reasonable and practical approach for most coals, and many other solid fuels, and has been applied for biomass ash analysis.

See also: Biomass.

Ash Content – Biomass

Ash content (which represents inorganic content) of biomass is the inorganic oxides that remain after complete combustion of the feedstock. The amount of ash between different types of feedstocks differs widely (0.1% for wood up to 15% for some agricultural products) and influences the design of the reactor, particularly the ash removal system. The chemical composition of the ash is also important because it affects the melting behavior of the ash. Ash melting can cause slagging and channel formation in the reactor. Slag can ultimately block the entire reactor.

Generally, the ash-forming inorganic materials in most solid fuels, including biomass, can be divided into two broad fractions, viz: (i) the inherent inorganic material and (ii) the extraneous inorganic material.

The inherent inorganic material, which exists as part of the organic structure of the fuel, and is most commonly associated with the oxygen-, sulfur-, and nitrogen-containing functional groups. These organic functional groups can provide suitable sites for the inorganic species to be associated chemically in the form of cations or chelates. Biomass materials tend to be relatively rich in oxygen-containing functional groups, and a significant fraction of the inorganic material in some of the lower ash biomass fuels is commonly in this form. It is also possible for inorganic species to be present in fine particulate form within the organic structure of some of the fuels, and to behave essentially as an inherent component of the fuel.

The extraneous inorganic material, which has been added to the fuel through geological processes, or during harvesting, handling, and processing of the fuel. Biomass fuels, for instance, are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling and storage.

The most commonly applied technique for the determination of the ash content and ash composition of coals and other solid fuels in the laboratory involve heating the fuel slowly in air to constant mass at a temperature of 815°C (1,500°F), and subjecting the resultant ash residue to chemical elemental analysis. The ash residue is normally weighed to provide an estimate of the ash content of the fuel, and then analyzed for the 10 major elements present in coal ashes, i.e., Si, Al, Fe, Ca, Mg, Ti, Na, K, P, and S. The elemental concentrations are conventionally expressed as oxides, in their highest oxidation states. The analysis of the laboratory-prepared ash for its trace element content is also fairly common practice. This is a perfectly reasonable and practical approach for most coals, and many other solid fuels, and has been applied for biomass ash analysis.

Biomass feedstocks and fuels exhibit a wide range of physical and chemical properties (Table A-25), but despite the wide range of possible sources, biomass feedstocks are remarkably uniform in many of their fuel properties. However, nearly all kinds of biomass feedstocks destined for combustion fall in the range 6,450 to 8,200 Btu/lb). For most agricultural residues, the heating values are even more uniform – approximately 6,450 to 7,300 Btu/lb. The values for most woody materials fall into the range 7,750 to 8,200 Btu/lb.

The most commonly applied technique for the determination of the ash content and ash composition of coals and other solid fuels in the laboratory involves heating the fuel slowly in air to constant mass at a temperature of 815°C (1,500°F), and subjecting the resultant ash residue to chemical elemental analysis. The ash residue is normally weighed to provide an estimate of the ash content of the fuel, and then analyzed for the 10 major elements present in coal ashes, i.e. Si, Al, Fe, Ca, Mg, Ti, Na, K, P, and S. The elemental concentrations are conventionally expressed as oxides, in their highest oxidation states. The analysis of the laboratory-prepared ash for its trace element content is also fairly common practice. This is a perfectly reasonable and practical approach for most coals, and many other solid fuels, and has been applied for biomass ash analysis.

See also Ash, Ash Composition.

As-Received Moisture

The as-received moisture of a carbonaceous samples is the moisture present in a sample when delivered to the analytical laboratory or to the customer. Moisture content can affect the self-heating rate of the sample in two ways: changing the overall heat balance and the rate of the oxidation reaction.

It has been suggested that there is a critical moisture content at which the rate of oxidation reached a maximum, but the reaction may be subject to the means of conducting the test which can change the subsequent low-temperature oxidation behavior of the sample.

Atmosphere

The atmosphere is the envelope of gases surrounding the earth, and it is subdivided into regions depending on the altitude. The constituents of the atmosphere are primarily nitrogen (N_2 , 78.08% v/v), oxygen (O_2 , 20.95% w/w), and water vapor (0 to 0.25% w/w), although the concentration of water vapor (H_2O) is highly variable, especially near the surface, where volume fractions can be as high as 4% in the tropics. There are many minor constituents or trace gases such as (alphabetically rather than by abundance, which is variable) argon (Ar), carbon dioxide (CO_2), helium (He), hydrogen (H_2), krypton (Kr), methane (CH_4), (neon, Ne), nitrous oxide (N_2O), ozone (O_3), and water vapor (H_2O) (Table A-26).

Table A-26 Approximate Composition of the Atmosphere.

Component, % v/v	Amount, % v/v
Major components:	
Nitrogen (N_2)	78.08
Oxygen (O_2)	20.95
Minor/trace components:	
Argon (Ar)	0.93
Water vapor (H_2O)	0.025*
Carbon dioxide (CO_2)	0.035
Neon (Ne)	0.018
Helium (He)	0.00052
Methane (CH_4)	0.00014
Krypton (Kr)	0.00010
Nitrous oxide (N_2O)	0.00005
Hydrogen (H_2)	0.00005
Ozone (O_3)	0.0000007

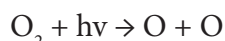
*Variable; can be as high as 4% v/v in humid areas.

In addition to the gaseous constituents, the atmosphere also contains suspended solid and liquid particles. Aerosols are particulate matter usually less than 1 micron in diameter (also called $1\ \mu m$ which is equivalent to $1\ m \times 10^{-6}$ in diameter, i.e., one millionth of a meter or one thousandth of a millimeter, 0.001 mm, or approximately 0.000039 of an inch) that are created by gas-to-particle reactions and are lifted from the surface by the winds. A portion of these aerosols can become centers of condensation or deposition in the growth of water and ice clouds. Cloud droplets and ice crystals are made primarily of water with some trace amounts of particles and dissolved gases. Their diameters

range up to 100 μm . Water or ice particles larger than approximately 100 microns begin to fall because of gravity and may result in precipitation at the surface.

Ozone is found in trace quantities throughout the atmosphere, the largest concentrations being location in a layer in the lower stratosphere between the altitudes of 9 and 18 mi (15 and 30 km). This ozone results from the dissociation by solar ultraviolet radiation of molecular oxygen in the upper atmosphere and nitrogen dioxide in the lower atmosphere. Ozone also plays an important role in the formation of photochemical smog and in the purging of trace species from the lower atmosphere.

The chemistry of ozone formation can be explained in relatively simple terms, although the reactions are believed to be much more complex. Thus, above approximately 19 mi (30 km), oxygen is dissociated during the daytime by energy ($h\nu$) from ultraviolet light:



The oxygen atoms produced then form ozone:



In this equation, M is an arbitrary molecule required to conserve energy and momentum in the reaction that produces ozone. Although present in only trace quantities (Table A-26), atmospheric ozone plays a critical role for the biosphere by absorbing the ultraviolet radiation with a wavelength from 240 to 320 nm (nm, 1 nm = 1 meter $\times 10^9$, which would otherwise be transmitted to the surface of the Earth.

The atmospheric ozone should not be confused with the ozone layer which acts as a region of stratosphere of the Earth that absorbs most of the ultraviolet radiation from the Sun. The ozone layer is mainly found in the lower portion of the stratosphere, from approximately 9 to 22 mi above the Earth, although the thickness of the layer varies seasonally and geographically. This layer is so-named because it contains a high concentration of ozone (O_3) in relation to other parts of the atmosphere, although still small in relation to other gases in the stratosphere. The ozone layer contains up to 10 parts per million of ozone, while the average ozone concentration in the atmosphere of the Earth as a whole is on the order of 0.3 parts per million.

The ultraviolet radiation is lethal to simple unicellular organisms (algae, bacteria, protozoa) and to the surface cells of higher plants and animals. It also damages the genetic material of cells (deoxyribonucleic acid, DNA) and is responsible for sunburn in human skin. In addition, the incidence of skin cancer has been statistically correlated with the observed surface intensities of the ultraviolet wavelengths from 290 to 320 nm, which are not totally absorbed by the ozone layer.

Atmospheric pressure decreases as an approximately exponential function of altitude, which largely determines the characteristics of the atmosphere. Thus:

$$P_h = P_o e^{mgh/RT}$$

In this equation, P_h is the pressure at any given height, P_o is the pressure at zero altitude (sea level); m is the average gram molecular mass of air (28.97 g/mole in the troposphere); g is the acceleration of gravity (981 $\text{cm} \times \text{sec}^{-1}$ at sea level); h is the altitude (in cm or meters or kilometers), and R is the gas constant (8.314 $\times 10^7 \text{ erg} \times \text{deg}^{-1} \times \text{mole}^{-1}$), and T is the absolute temperature. Furthermore:

$$\log P_h = \log P_o - (mgh \times 10^5)/2.303RT$$

At sea level where the pressure is 1 atm:

$$\log P_h = (mgh \times 10^5)/2.303RT$$

The characteristics of the atmosphere vary widely with altitude, time (season), location (latitude), and even solar activity. At a high altitude, normally reactive species, such as atomic oxygen, persist for long periods of time. At such

altitudes, the pressure is low and the distance traveled by a reactive species before it collides with a potential reactant (the mean free path) is high.

An important effect noted as a result of the changes in the constituents of the atmosphere is the tendency for the temperature close to the surface of the Earth to rise, a phenomenon referred to as the greenhouse effect. This term is used to describe the rise in the temperature of the earth, analogous to the rise in temperature in a greenhouse when the energy from the sun is trapped and cannot escape from the enclosed space. Although the term greenhouse effect has generally been used for the role of the whole atmosphere (mainly water vapor and clouds) in keeping the surface of the earth warm, it has been increasingly associated (perhaps erroneously) with the contribution of carbon dioxide. However, there are various types of gases that are the result of industrial and domestic activities that can contribute to this effect and, thus, the continual rise in the surface temperature of the earth.

The arguments related to the magnitude of the greenhouse effect have ranged back and forth for some time with carbon dioxide as the main (if not the sole) cause without recognition of other causes, several of which are natural causes or events. There are those who believe that the Earth is doomed to a rise in temperature and serious harm to the human race is imminent. On the other hand, there are those observers who believe that there is no cause for concern related to the environment and humans can go on merrily as has been the case for centuries and polluting the atmosphere without any concerns related to the consequences of such actions. Whatever the correct side on which to base an argument, there is no doubt that the emissions, which can give rise to such an effect, must be limited. The continuous pollution of the atmosphere with the so-called greenhouse gases can be of no advantage to life on earth, even if the effects of these gases are not manifested in a temperature rise but in the form of aggravating pollutants to flora and fauna.

Both of these opposite opinions are of some concern because they may mask the reality of the situation. It is analogous to other situations that have arisen in the last several decades. For example, in the late 1960s and early 1970s, there were warnings related to an approaching ice age. In fact, they were those observers who would have us believe that, upon looking out of the window, an observer(s) would see glaciers approaching from the end of the street! In fact, it is entirely likely that several important analysts who then warned of global cooling and imminent glaciation of northern societies are now warning of global warming. The glaciers did not arrive and now, in a little more fifty years later, the frantic warnings are not related to a rise in global temperature! There are also advisories that the rise in temperature that is the basis of global warming is being accompanied (perceived or real) by the emergence (or reemergence) of a variety of infectious diseases. If, as has been suggested, the Earth has warmed 0.3 to 0.6°C (approximately 1°F, or less) during this century, the perception is that a higher rise in the temperature of the earth may lead to a series of global catastrophes.

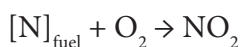
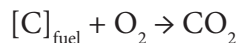
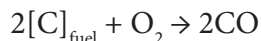
These types of contradictory reports and arguments add much confusion to an already difficult area of technology. It seems that every time a government appropriates money to study an issue, the heretofore unheard-of-experts spring into action. What is really needed is a careful study of the data, the generation of new data, and less enthusiasm for catching the headlines.

Chemicals can be emitted directly into the atmosphere or formed by chemical conversion through chemical reactions of precursors species. In these reactions, highly toxic chemicals can be converted into less toxic products, but the result of the reactions can also be products having a higher toxicity than the starting chemicals. In order to understand these reactions, it is also necessary to understand the chemical composition of the natural atmosphere, the way gases, liquids, and solids in the atmosphere interact with each other and with the surface of the Earth and associated biota, and how human activities may be changing the chemical and physical characteristics of the atmosphere.

There are a number of critical environmental issues associated with a changing atmosphere, including photochemical smog, global climate change, toxic air pollutants, acidic deposition, and stratospheric ozone depletion. Much of the anthropogenic (human) impact on the atmosphere is associated with the increasing use of fossil fuels as an energy source – for things such as heating, transportation, and electric power production. Photochemical smog/tropospheric ozone is a serious environmental problem that has been associated with burning such fuels, and the result has been the formation and deposition of acid rain.

Acid rain is formed when sulfur oxides and nitrogen oxides react with water vapor and other chemicals in the presence of sunlight to form various acidic compounds in the atmosphere. The principal source of acid rain-causing

pollutants, sulfur oxides and nitrogen oxides, is from fuel combustion – specifically from fuels that contain sulfur and nitrogen:



sulfurous acid



sulfuric acid



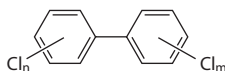
nitrous acid



nitric acid

Two of the pollutants that are emitted are hydrocarbon derivatives (e.g., unburned fuel) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which the NO is converted to nitrogen dioxide (NO₂) – a brown gas and at sufficiently high levels can contribute to urban haze. However, a more serious problem is that nitrogen dioxide (NO₂) can absorb sunlight and break apart to produce oxygen atoms that combine with the oxygen in the air to produce ozone (O₃), a powerful oxidizing agent, and a toxic gas.

In addition, as a result of a variety of human activities (e.g., agriculture, transportation, industrial processes) a large number of different toxic chemical pollutants are emitted into the atmosphere. Among the chemicals that may pose a human health risk are pesticides, polychlorobiphenyl derivatives (PCBs), polycyclic aromatic hydrocarbon derivatives (PAHs), dioxin derivatives, and volatile compounds (e.g., benzene, carbon tetrachloride).



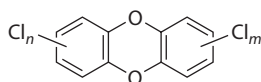
Polychlorobiphenyl derivatives; *n* and *m* can be any number from 1 to 5.



1,4-Dioxin



1,2-Dioxin



Polychlorinated dibenzo-p-dioxin derivatives; n and m can be any number from 1 to 5.

Many of the more environmentally persistent compounds (such as the polychlorobiphenyl derivatives) have been measured in various floral and faunal species.

See also: Condensation.

Atmospheric Equivalent Boiling Point

The atmospheric equivalent boiling point is the boiling point at which a sample or fraction of a fuel would boil under atmospheric pressure if it was stable and would not decompose. This provides a common basis for the categorization and direct comparison of petroleum components across the entire volatility range accessible by atmospheric and vacuum distillation.

Distillation at lower pressure allows high-boiling fractions to distill at lower temperatures, thereby foregoing the potential of thermal decomposition if attempts were made to distill the fraction at the higher temperatures required at atmospheric pressure. This allows the collection of distillates with an atmospheric equivalent temperature cut point of as high as 560°C (1050°F). The actual observed boiling points during this distillation are, of course, much lower. Despite the low pressure, the reboiler may have to be heated as high as 370°C (700°F) for such high-boiling distillates.

Molecular distillation is a non-equilibrium process and the atmospheric equivalent boiling range of a fuel or a fraction of a fuel that cannot be measured directly. The atmospheric equivalent boiling point (AEBP) concept was developed to compensate for this and can be estimated from one of the following equations:

$$\text{mid-AEBP } (^{\circ}\text{F}) = \{[(M_n - 140)(\text{sp. gr.})^{2.5/3.40}] \times 10^7\}^{1/3}$$

$$\text{mid-AEBP } (^{\circ}\text{F}) = \{[(M_n - 170)(\text{H/C})^{0.9/2.67}] \times 10^7\}^{1/3}$$

The mid-AEBP is the temperature for the 50% mass point on the distillation curve of the fraction, and M_n is the molecular weight. Either the specific gravity (sp. gr.) or atomic hydrogen/carbon (H/C) ratio, which can be readily measured in the fractions, can also be used. Using the mid-AEBP concept, even fractions of the non-distillable residue can be included in the boiling range curves and relationships such as the variation of sulfur and nitrogen contents can be derived as a function of the AEBP.

Typically, as the mid-AEBP increases, the sulfur and nitrogen concentrations of the fraction generally also increase. Also, the highest concentrations of both sulfur and nitrogen appear in the non-distillable fractions. This behavior follows the heteroatom behavior observed for refinery distillation cuts. Thus, the higher the boiling range of the fraction, the higher the heteroatom concentration. This also establishes that the heteroatom concentration continues to increase as the volatility of the compounds decreases, which was not known previously for the 540°C⁺ (1000°F⁺) residuum.

Atomic Energy

Atomic energy (or, more correctly, nuclear energy) is a term that represents the energy with an atom and includes (i) nuclear binding energy, (ii) nuclear potential energy, (iii) nuclear reaction, which is a process in which nuclei

or nuclear particles interact, resulting in products different from the initial ones, (iv) radioactive decay which is a descriptor for the various processes by which unstable atomic nuclei (nuclides) emit subatomic particles, and (iv) the energy of inter-atomic or chemical bonds, which holds atoms together in compounds.

Atomic energy is the source of nuclear power which uses sustained nuclear fission to generate heat and electricity. It is also the source of the explosive force of an atomic bomb. The energy originates from the splitting of uranium atoms (nuclear fission) which generates heat to produce steam, which is used by a turbine generator to generate electricity. Because nuclear power plants do not burn fuel, they do not produce greenhouse gas emissions but, caution is advised, and although the risk of accidents in nuclear power plants is low, the consequences of an accident can be drastic and highly detrimental to the surrounding flora and fauna (including human life).

See also: Nuclear Energy, Nuclear Fission, Nuclear Fusion.

Attapulgius Clay

Attapulgius clay (*attapulgiite* or *palygorskite*) is a magnesium aluminum phyllosilicate $[(\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}\cdot 4\text{H}_2\text{O}]$ which occurs in a type of clay soil common to the Southeastern United States. It is one of the types of fuller's earth.

The name *attapulgiite* is derived from the U.S. town of Attapulgius, Georgia, in the extreme southwest corner of the state, where the mineral is abundant. It is surface-mined in the area, dry-ground and air-separated into precise particle sizes, and transported in covered hopper cars via the railroad, and is also shipped in 50-lb bags and bulk bags by truck. The name *palygorskite* is given after the place in the Ural Mountains where it was discovered.

Attapulgiite clays are swellable clays like bentonite, although more acicular (or needle like). Attapulgiite, unlike bentonite, will swell in salt water and is used in special salt water drilling mud for off shore oil drilling. Like many clays, they can be considered as charged particles with zones of positive and negative charges. Standard attapulgiite clays are agglomerated bundles of clay particles between 20 and 100 μm long and below 1 μm in diameter. Most grades contain up to 25% non-attapulgiite material in the form of mineral carbonates and other inclusions. The advantage of attapulgiites is that their performance is not temperature sensitive and they have lower water demand. They must have free ions in an aqueous system to work.

See also: Clay Minerals, Clay Treating Process.

Attrition Catalyst

Typically, a relatively inexpensive catalyst that is designed to remove impurities and unwanted by-products from gas streams which, at the same time, is sacrificed. For example, alumina (Al_2O_3) guard beds serve as protectors by the act of attrition and may be referred to as an attrition reactor containing an attrition catalyst may be placed ahead of the molecular sieves to remove the sulfur compounds. Downflow reactors are commonly used for adsorption processes, with an upward flow regeneration of the adsorbent and cooling using gas flow in the same direction as adsorption flow.

See also: Guard Bed, Guard Bed Reactor.

Azeotrope

Two main types of azeotropes exist, i.e., the *homogeneous azeotrope*, where a single liquid phase is in the equilibrium with a vapor phase; and the *heterogeneous azeotropes*, where the overall liquid composition which form two liquid phases, is identical to the vapor composition. Most methods of distilling azeotropes and low relative volatility mixtures rely on the addition of specially chosen chemicals to facilitate the separation.

The five methods for separating azeotropic mixtures are: (i) extractive distillation and homogeneous azeotropic distillation where the liquid separating agent is completely miscible, (ii) heterogeneous, (iii) azeotropic distillation, or more commonly, azeotropic distillation where the liquid separating agent (the entrained) forms one or more azeotropes with the other components in the mixture and causes two liquid phases to exist over a wide range of

compositions – this immiscibility is the key to making the distillation sequence work, (iv) distillation using ionic salts in which the salts dissociate in the liquid mixture and alters the relative volatilities sufficiently that the separation become possible, (iv) pressure-swing distillation in which a series of column operating at different pressures are used to separate binary azeotropes which change appreciably in composition over a moderate pressure range or where a separating agent which forms a pressure-sensitive azeotrope is added to separate a pressure-insensitive azeotrope, and (v) reactive distillation where the separating agent reacts preferentially and reversibly with one of the azeotropic constituents; the reaction product is then distilled from the non-reacting components, and the reaction is reversed to recover the initial component, (v) simple distillation in which a multi-component liquid mixture is slowly boiled in a heated zone and the vapors are continuously removed as they form and, at any instant in time, the vapor is in equilibrium with the liquid remaining on the still; because the vapor is always richer in the more volatile components than the liquid, the liquid composition changes continuously with time, becoming more and more concentrated in the least volatile species.

A simple distillation residue curve is a means by which the changes in the composition of the liquid residue curves on the pot changes over time. Residue curve map is a collection of the liquid residue curves originating from different initial compositions. Residue curve maps contain the same information as phase diagrams, but represent this information in a way that is more useful for understanding how to synthesize a distillation sequence to separate a mixture.

All of the residue curves originate at the light (lowest boiling) pure component in a region, move toward the intermediate boiling component, and end at the heavy (highest boiling) pure component in the same region. The lowest temperature nodes are termed as unstable nodes, as all trajectories leave from them, while the highest temperature points in the region are termed stable nodes, as all trajectories ultimately reach them. The point that the trajectories approach from one direction and end in a different direction (as always is the point of intermediate boiling component) is termed saddle point. Residue curves that divide the composition space into different distillation regions are called distillation boundaries.

The separation of components of similar volatility may become economical if an *entrainer* can be found that effectively changes the relative volatility. It is also desirable that the entrainer be reasonably cheap, stable, non-toxic, and readily recoverable from the components. In practice, it is probably this last criterion that severely limits the application of extractive and azeotropic distillation. The majority of successful processes, in fact, are those in which the entrainer and one of the components separate into two liquid phases on cooling if direct recovery by distillation is not feasible.

A further restriction in the selection of an azeotropic entrainer is that the boiling point of the entrainer be in the range 10 to 40°C (18 to 72°F) below that of the components. Thus, although the entrainer is more volatile than the components and distills off in the overhead product, it is present in a sufficiently high concentration in the rectification section of the column.

See also: Azeotropic Distillation, Distillation.

Azeotropic Distillation

Azeotropic distillation is the use of a third component to separate two close-boiling components by means of the formation of an azeotropic mixture between one of the original components and the third component to increase the difference in the boiling points and facilitates separation by distillation.

All compounds have definite boiling temperatures, but a mixture of chemically dissimilar compounds sometimes causes one or both of the components to boil at a temperature other than that expected. For example, benzene boils at 80°C (176°F), but if it is mixed with hexane, it distills at 69°C (156°F). A mixture that boils at a temperature lower than the boiling point of either of the components is called an azeotropic mixture.

Chemical bonding between the components of the mixture creates properties unique to the mixture. If the system forms azeotropes, as in a benzene and cyclohexane system, a different problem arises - the azeotropic composition limit the separation, and for a better separation, this azeotrope must be bypassed in some way. At the azeotropic point, the mixture contains the given component in the same proportion as the vapor, so that evaporation does not

change the purity, and distillation does not affect separation. For example, ethyl alcohol and water form an azeotrope (azeotropic mixture) at 78.2°C (172.8°F).

If the separation of individual components from petroleum itself or from petroleum products is required, there are means by which this can be accomplished. For example, when a constant-boiling mixture of hydrocarbons contains components whose vapor pressure is affected differently by the addition of, say, a non-hydrocarbon compound, distillation of the hydrocarbon mixture in the presence of non-hydrocarbon additive may facilitate separation of the hydrocarbon components.

In general, the non-hydrocarbon additive is a polar organic compound and should also have the ability to form a binary minimum constant-boiling (or azeotropic) mixture with each of the hydrocarbons. Thus, it is often possible to separate compounds that have close boiling points by means of azeotropic distillation.

See also: Azeotrope, Distillation.

Bacteria

Bacteria are microscopic, single-celled organisms that thrive in diverse environments. These organisms can live in soil, the ocean, and inside the human digestive system. Bacteria are classified into five groups according to their basic shapes: (i) spherical shapes, also known as cocci, (ii) rod shapes, also known as bacilli, (iii) spiral shapes, also known as spirilla, (iv) comma shapes, also known as vibrios, and (v) corkscrew shapes, also known as spirochaetes which can also exist as single cells, in pairs, chains, or clusters.

Bacteria occur individually or grow as groups ranging from two to millions of individual cells. Individual bacteria cells are small and may be observed only through a microscope. Most bacteria fall into the size range of 0.5 to 3.0 microns ($1 \text{ micron} = 1 \text{ m} \times 10^{-6}$). However, considering all species, a size range of 0.3-50 microns is observed. In general, it is assumed that a filter with a pore size on the order of 0.45 micron will remove all bacteria from water passing through it.

The metabolic activity of bacteria is greatly influenced by their small size. Their surface-to-volume ratio is extremely large, so that the inside of a bacterial cell is accessible to a chemical substance in the surrounding medium. Thus, for the same reason that a finely divided catalyst is more efficient than a more coarsely divided one, bacteria may cause rapid chemical reactions compared to those mediated by larger organisms. Bacteria excrete enzymes that can act outside the cell (exoenzymes) that break down solid food material to soluble components which can penetrate bacterial cell walls, where the digestion process is completed.

Bacteria obtain the energy needed for their metabolic processes and reproduction by mediating redox reactions. Nature provides a large number of such reactions, and bacterial species have evolved that utilize many of these. As a consequence of their participation in such reactions, bacteria are involved in many biochemical processes in water and soil.

Bacteria are essential participants in many important elemental cycles in nature, including those of nitrogen, carbon, and sulfur. They are responsible for the formation of many mineral deposits, including some of iron and manganese. On a smaller scale, some of these deposits form through bacterial action in natural water systems and even in pipes used to transport water.

The presence of coliform bacteria, specifically *E. coli* (a type of coliform bacteria), in drinking water suggests the water may contain pathogens that can cause a variety of diseases and even death.

See also: Bacterial Mining.

Bacterial Mining

Bacterial mining, or bio-mining, represents the use of microorganisms to leach metals from ores or mine tailings (wastes), followed by the subsequent recovery of metals of interest from the leaching solution. The term has also been applied to the recovery of oil from reservoirs where the reservoir energy has been depleted over time. This could well be a process of the future for recovering energy from alternate sources that have been difficult-to-impossible to reach or recover and develop.

The use of microbes to extract metals from ores is simply the harnessing of a natural process for commercial purposes. Microbes have participated in the deposition and solubilization of heavy metals in the earth's crust since geologically ancient times. Most of this activity is linked to the iron and sulfur cycles. Anaerobic sulfate reducing bacteria generate sulfides that can react with a variety of metals to form insoluble metal sulfides. There are two main types of processes for commercial-scale microbially assisted metal recovery. These are irrigation-type and stirred tank-type processes. Bio-mining involves a chemical process called leaching which is actually oxidation reaction and maybe called bio-oxidation. Bio-leaching processes can be carried out at a range of temperatures, and as would be

expected, the iron- and sulfur-oxidizing microbes present differ depending on the temperature ranges. In mineral bio-oxidation processes that operate at 40°C or less, the most important microorganisms are believed to be a consortium of gram-negative bacteria such as *Acidithiobacillus ferrooxidans*. Microorganisms that dominate bio-leaching at 50°C (122°F) include *Acidithiobacillus caldus* and some *Leptospirillum* spp. At temperatures greater than 65°C (149°F), bio-mining microbial consortia are dominated by archaea rather than bacteria with species of *Sulfolobus* and Metallophores being most prominent.

Thus, biomining has developed into a successful and expanding area of biotechnology and the process employs microbial consortia that are dominated by acidophilic, autotrophic iron- or sulfur-oxidizing prokaryotes. Mineral bio-oxidation takes place in highly aerated, continuous-flow, stirred-tank reactors or in irrigated dump or heap reactors, both of which provide an open, non-sterile environment. Continuous-flow, stirred tanks are characterized by homogeneous and constant growth conditions where the selection is for rapid growth, and consequently, tank consortia tend to be dominated by two or three species of microorganisms. In contrast, heap reactors provide highly heterogeneous growth environments that change with the age of the heap, and these tend to be colonized by a much greater variety of microorganisms. Heap microorganisms grow as biofilms that are not subject to washout, and the major challenge is to provide sufficient biodiversity for optimum performance throughout the life of a heap.

Currently, a variety of biotechnological processes are being given serious consideration as options to the more conventional recovery methods for energy production. During the energy crisis that commenced in the 1970s, a bioleaching process was applied to oil shale in the United States in order to produce shale oil. Sulfur is actually introduced to the fractured oil shale blocks, and *Thiobacilli thiooxidans* is used to generate a large amount of 0.1 N sulfuric acid to remove carbonate minerals. With Green River oil shale, 43% of the carbonates can be removed so that a more porous oil shale rock will remain. More oil can be produced from this treatment method due to the improved heat transfer efficiency upon retorting.

See also: Bacteria.

Bagasse

Bagasse is the dry pulpy residue left after the extraction of juice from sugar cane, used as fuel for electricity generators and other forms of energy. In addition, bagasse is 100% compostable, and if it does enter our environment, it will break down into soil entirely naturally, without any human intervention or additional processing.

More specifically, bagasse is the fibrous residue remaining after sugarcane or sorghum stalks are crushed to extract their juice and is currently used as a renewable resource in the manufacture of pulp and paper products and building materials. Bagasse is often used as a primary fuel source for sugar mills; when burned in quantity, it produces sufficient heat energy to supply all the needs of a typical sugar mill, with energy to spare. To this end, a secondary use for this waste product is in cogeneration, the use of a fuel source to provide both heat energy, used in the mill, and electricity, which is typically sold to the consumer electricity grid.

Sugarcane bagasse is the major by-product of the sugar cane industry and contains approximately 50% w/w cellulose, 25% w/w hemicellulose, and 25% w/w lignin. Due to its abundant availability, the bagasse can serve as an ideal substrate for microbial processes for the production of value-added products such as protein-enriched animal feed, enzymes, amino acids, organic acids, and compounds of pharmaceutical importance.

The utilization of organic and agricultural residues such as bagasse for energy production is considered an important part in any strategy to achieve renewable energy goals and to reduce waste disposal and environmental pollution. For energy production, bagasse can be burned as a raw product or in the form of briquettes. Currently, most sugar cane bagasse is burned in boilers to produce steam which is utilized in factories and to power turbines for the production of electricity (cogeneration).

The combustion of sugar cane bagasse yields ash (bottom ash and fly ash) that contains high amounts of organic matter (charcoal and sugar cane bagasse debris) and inorganic components (on the order of 65% w/w).

One of the significant applications of bagasse is the production of protein-enriched cattle feed and enzymes. Bagasse could also be used for the production of industrially important enzymes and biofuel.

See also: Agave Bagasse, Bagasse Briquettes, Biomass, Sugarcane, Sugar Crops, Sugars and Starch.

Bagasse Briquettes

Bagasse is the fibrous residue remaining after sugarcane or sorghum stalks, for example, are crushed to extract their juice. It is currently used as a renewable resource in the manufacture of pulp and paper products and building materials. However, surplus bagasse presents a disposal problem for many sugar factories. Briquetting technology offers a way to reduce the surplus amount of bagasse.

A briquette (also spelled briquet) is a compressed block of (typically) combustible material (such as charcoal, sawdust, and wood chips) used for fuel. In some cases, the briquettes may be used for transportation before further processing. A piston press is used to create solid briquettes for a wide array of purposes. Screw extrusion is used to compact biomass into loose, homogeneous briquettes that are substituted for coal in cofiring. This technology creates a toroidal (doughnut-like) briquette.

The briquetting process involves the following steps: (i) size reduction in which the bagasse is chopped, rolling, or hammered, (ii) drying in which moisture is removed by open air drying or by using forced, heated air in a large rotating drum, (iii) carbonization in which the bagasse is combusted in a limited supply of oxygen in a buried pit or trench until it carbonizes into charcoal, (iv) feedstock preparation in which the carbonized bagasse is mixed with a binder such as clay or molasses, (v) compaction and extrusion in which the material is passed through a machine-operated or manually-operated extruder to form rolls of charcoal, (vi) drying in which the rolls are air-dried for 1 to 3 days, causing them to break into chunks, and (vii) packaging in which the briquettes are made ready for sales.

See also: Agave Bagasse, Bagasse.

Baghouse

The baghouse (also known as a baghouse filter, bag filter, fabric filter, or fabric collector) uses filtration to separate dust particulates from particle-laden gases. They are one of the most efficient and cost-effective types of dust collectors available and can achieve a collection efficiency of more than 99% for fine particulates. A baghouse can be engineered for almost any dust producing application under almost any set of circumstances. In the cleaning process, particle-laden gases enter the baghouse and pass through a series of fabric bags that act as filters. The bags can be made of woven or felted cotton, synthetic, or glass-fiber material in either a tube or envelope shape.

The high efficiency of these collectors is due to the dust cake formed on the surfaces of the bags. The fabric primarily provides a surface on which dust particulates collect through the following mechanisms which are (i) inertial collection in which dust particles strike the fibers placed perpendicular to the gas-flow direction instead of changing direction with the gas stream, (ii) interception in which particles that do not cross the fluid streamlines come in contact with fibers because of the fiber size, and (iii) electrostatic forces in which the presence of an electrostatic charge on the particles and the filter can increase dust capture. A combination of these mechanisms results in formation of the dust cake on the filter, which eventually increases the resistance to gas flow. The filter must be cleaned periodically.

Baghouses come in design classifications based on the manner by which the bags are cleaned: (i) the pulse jet system, which uses high-pressure air directed down into the clean side of a filter bag in order to remove the dust cake from the surface of the media, (ii) the shaker style system, which involves shaking the bags in order to mechanically release the dust cake, and (iii) the reverse air system in which the bags are collapsed in order to mechanically shear the dust cake from the bag surface.

In mechanical-shaker baghouses, tubular filter bags are fastened onto a cell plate at the bottom of the baghouse and suspended from horizontal beams at the top. The contaminate gas streams enters the bottom of the baghouse and passes through the filter, and the dust collects on the inside surface of the bags. Cleaning a mechanical-shaker baghouse is accomplished by shaking the top horizontal bar from which the bags are suspended. Vibration produced by a motor-driven shaft and cam creates waves in the bags to shake off the dust cake.

In reverse-air baghouses, the bags are fastened onto a cell plate at the bottom of the baghouse and suspended from an adjustable hanger frame at the top. Dirty gas flow normally enters the baghouse and passes through the bag from

the inside, and the dust collects on the inside of the bags. In reverse-jet baghouses, individual bags are supported by a metal cage, which is fastened onto a cell plate at the top of the baghouse. Dirty gas enters from the bottom of the baghouse and flows from outside to inside the bags. The metal cage prevents collapse of the bag. Bags are cleaned by a short burst of compressed air injected through a common manifold over a row of bags. The compressed air is accelerated by a venturi nozzle mounted at the reverse-jet baghouse top of the bag. Since the duration of the compressed-air burst is short (0.1 seconds), it acts as a rapidly moving air bubble, traveling through the entire length of the bag and causing the bag surfaces to flex. This flexing of the bags breaks the dust cake, and the dislodged dust falls into a storage hopper below.

Cartridge collectors are another commonly used type of dust collector. Unlike baghouse collectors, in which the filtering media is woven or felt bags, this type of collector employs perforated metal cartridges that contain a pleated, nonwoven filtering media. Due to its pleated design, the total filtering surface area is greater than in a conventional bag of the same diameter, resulting in reduced air-to-media ratio, pressure drop, and overall collector size.

See also: Baghouse Filter.

Baghouse Filter

Baghouse fabric filters are generally used where higher removal efficiency is required for particles smaller than approximately 10 microns. Thus, the filter is an air pollution control device and dust collector that removes particulates or gas released from commercial processes. A large number of bag-shaped filters would be needed to clean large gas flows. In general, all of the filters would be enclosed in the same structure (a *baghouse*) and would share input and output gas manifolds.

As a gas stream passes through the baghouse, dust is removed by one or more of the following physical phenomena: intersection, impingement, diffusion, gravitational settling, or electrostatic attraction. The initial filtration creates a layer of dust on the bag fabric. This layer is primarily responsible for this method's high removal efficiency; the filter cloth serves mainly as a support structure.

The efficiency of a baghouse filter depends on the particle size distribution, the particle density and chemistry, and moisture. Under most conditions, a well-designed and well-operated baghouse will achieve a removal efficiency of at least 99% for particles as small as 1 micron. In the renewable energy industry, baghouse filters are likely to be used for dust removal from crushers, screens, transfer points, and storage bins.

Fabric life may be substantially shortened in the presence of high acid or alkaline atmospheres, especially at elevated temperatures; also, the maximum operating temperature is limited to 285°C (550°F), unless special fabrics are used.

See also: Baghouse, Centrifugal Separation, Cyclone Separation.

Barrel

The standard oil barrel of 42 US gallons is used in the United States as a measure of crude oil and other crude oil products. The 42 US gallon size of barrel as a unit of measure is largely confined to the American oil industry, since other sizes of barrel were used by other industries in the United States, and nearly all other countries use the metric system. Many oil-producing countries that did not have the technical expertise to develop their own domestic oil industry standards use the American oil barrel because their oil industries were founded by US oil companies.

Outside of the United States, oil is commonly measured in cubic meters (m³) or in tonnes (1 tonne = 2,204.6 lbs), with tonnes more often being used by European oil companies. International companies listed on American stock exchanges tend to convert their oil production volumes to barrels for global reporting purposes, and those listed on European exchanges tend to convert their production to tonnes.

The wooden oil barrel of the late 1800s is different from the modern day 55-gal steel drum (known as the 44-gal drum in Britain and the 200-L drum in Australia). The 42-US gallon oil barrel is a unit of measure, and is no longer used to transport crude oil – most crude oil is moved in pipelines or oil tankers.

The barrel of oil equivalent (BOE) is a unit of energy based on the approximate energy released by burning one barrel (42 US gallons) of crude oil. The Internal Revenue Service of the United States defines the barrel of oil equivalent as equal to 5.8×10^6 Btu. A barrel of oil equivalent is approximately 6,000 ft³ of typical natural gas.

Other conversion data are the BBOe, (also BBOE), or billion barrel of oil equivalent, representing 10⁹ (US billion) barrels of oil, used to measure crude oil reserves, and million barrels per day, MMbd (or MMBD), used to measure daily production and consumption. Also used is the Mtoe (not *middle toe* but *millions of tonnes of oil equivalent*), a metric measurement equivalent to approximately 0.006841 billion barrels of oil equivalent.

The barrel of oil equivalent is used by oil and gas companies in their annual financial statements as a way of combining oil reserves and natural gas reserves as well as production into a single measure.

See also: Barrel of Oil Equivalent.

Barrel of Oil Equivalent

A barrel of oil equivalent (BOE or a barrel of crude oil equivalent, BCOE) is used to summarize the amount of energy that is equivalent to the amount of energy found in a barrel of crude oil. Thus, a barrel of crude oil is a liquid measure equal to 42 US gallons (35 Imperial gallons or 158.9873 L). The BOE is the amount of energy contained in a barrel of crude oil; a barrel of crude oil is approximately (because of the difference in crude oil properties and character) equivalent to 5.8 million Btu. Also, approximately 7.2 barrels of oil are equivalent to one ton of oil. A BOE is approximately roughly 6,000 ft³ of natural gas.

A commonly used multiple of the BOE is the kilo-barrel of oil equivalent (kboe or kBOE), which is 1,000 times larger. Other common multiples are the billion BOE, representing 10⁹ barrels of oil, used to measure crude oil reserves, and million barrels per day (MMbd or MMBD), used to measure daily production and consumption. Also used is the million tons of oil equivalent (Mtoe) which is a metric measurement equivalent to approximately 0.006841 billion barrels of crude oil equivalent.

The BOE is used by oil and gas companies in their financial statements as a way of combining crude oil reserves and natural gas reserves and production into a single measure.

See also: Barrel, Resources And Reserves.

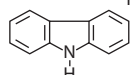
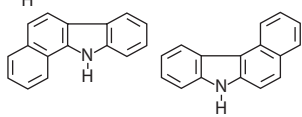
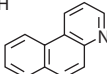
Basic Nitrogen

Nitrogen in liquid fuels (renewable fuels are included here) may be classified arbitrarily as basic and non-basic (Table B-1). The basic nitrogen compounds, which are composed mainly of pyridine-type homologs and occur throughout the boiling ranges of organic compounds, which are usually of the pyrrole, indole, and carbazole types, have a decided tendency to exist in the higher boiling fractions and crude oil residua and in liquids from alternative energy sources such as biomass and organic waste.

Organic nitrogen-containing compounds have many important roles in nature (hence, also in biomass) and display an enormous structural diversity, in which the nitrogen atoms can form part of simple functional groups or complex heterocyclic systems. The basic nitrogen compounds also have varying degrees of substitution and oxidation. The most noteworthy of these naturally occurring molecules are proteins, and most vitamins and hormones. Furthermore, nitrogen compounds in liquids produced from a variety of sources (including biomass and organic waste) can have a deleterious effect on any catalysts used to upgrade the liquid.

Basic nitrogen compounds with a relatively low molecular weight can be extracted with dilute mineral acids; equally strong bases of higher molecular weight remain unextracted because of unfavorable partitioning between the oil and aqueous phases. A method has been developed in which the nitrogen compounds are classified as basic or non-basic, depending on whether they can be titrated with perchloric acid in a 50:50 solution of glacial acetic acid and benzene.

Table B-1 Non-basic and basic nitrogen types.

Nonbasic		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Benzo(a)carbazole	$C_{16}H_{11}N$	
Basic		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Benzo(f)quinoline	$C_{13}H_9N$	

Nitrogen compounds extractable with dilute mineral acids from renewable fuels typically consist of alkyl pyridine derivatives, alkyl quinoline derivatives, and alkyl isoquinoline derivatives carrying alkyl substituents, as well as pyridine derivatives in which the substituent was a cyclopentyl or cyclohexyl group. The compounds that cannot be extracted with dilute mineral acids contain the greater part of the nitrogen in crude oil and are generally of the carbazole, indole, and pyrrole types.

Thus, the presence of the various types of nitrogen compounds in any feedstock must be monitored because they can critically affect aquatic ecosystems, especially their high levels can cause eutrophication under certain conditions. Ammonia, organic species, nitrate derivatives ($-NO_3$), and nitrite derivatives ($-NO_2$) can be present in wastewaters. In general, ammonia and organic species are the most common in raw water. Ammonia is the initial product of the decay of nitrogenous organic wastes, its presence being an indication of such wastes. Typically, the nitrate content in waters is low but can rise to appreciable levels in wastewater from agricultural activities as a result of soil fertilization. Also, nitrite derivatives are present in low concentration since these are rapidly oxidized to nitrates, while nitrite derivatives can be found in wastewaters from the microbiological reduction of nitrate or the oxidation of ammonia.

See also: Waste, Waste Disposal.

Basic Sediment and Water

The basic sediment and water (often referred to in a shortened form, such as BS&W, BSW) is the material which collects in the bottom of storage tanks and is usually composed of oil, water, and foreign matter, also called bottoms or bottom settlings. The material is also known as bottoms, bottom sediment, bottom settlings, sediment, and water.

The particulate matter is known as sediment or mud. The water content can vary greatly from fuel to fuel (conventional or alternate). The bulk of the water and sediment is usually separated as soon as possible after production to minimize the quantity that needs to be transported and/or transferred to subsequent processing units. Further, the residual content of these unwanted impurities is measured as bottom sediment and water (BS&W, ASTM D4007).

Thus, basic sediment and water are both a technical specification of certain impurities in any fuel and the method for measuring it. In many raw fuels (including fuels produced from biomass), the crude oil will contain some amount

of water and suspended solid from the starting material. The particulate matter and the water content can vary greatly from feedstock to feedstock and from process to process. The bulk of the water and sediment is usually separated at the earliest possible convenience to minimize the quantity that needs to be transported further as well as any adverse effects on the process and process equipment.

Upon production of a fuel from a renewable source, the fuel typically passes through facilities that allow gas and water to separate from the crude and solids to settle out. These facilities may comprise a simple gathering tank or a series of specialized separation vessels, and may involve the addition of chemicals to the crude to aid in the separation of various contaminants from the crude oil and natural gas.

The BS&W test has been used to determine composition of the fuel from many sources and should be tested frequently to ensure it meets the prescribed quality requirements. There are two tests conducted, a bottom sediment and water test (BS&W) and a visual test. The BS&W test is done at the beginning, mid-point, and end of the fuel production train. Visual tests are conducted every fifteen minutes during the evolution. The visual criteria is simply that the fuel be *clear and bright* and the test is a quick and easy check of the fuel quality.

See also: Refining.

Batch-Type Processes

A batch process is usually performed over and over, and batch processes are a sub-class of sequential processes. Batch process refers to a process that involves a sequence of steps followed in a specific order. Also, batch processes generate a product but the sequential processes need not necessarily generate a product. Thus, batch processing is a technique for automating and processing multiple portions of a feedstock. More generally, industrial processes can be divided into two categories of production which are (i) continuous processes and (ii) batch processes.

Continuous processes are designed to run at steady state, and to maximize the efficiency of these processes, it is necessary to keep the plant in the operating range under disturbances. The optimization task required to operate such processes is usually performed to achieve disturbance rejection, designing controllers to reach and maintain set-point effectively, and keeping the down time to a minimum. Since the operating range is generally very narrow, the system dynamics can often be approximated by linear dynamics.

Batch processes have a finite operating time, rather than a continuous operation. The control objective in batch processing is not to reach steady state, but to reach some desired objective by the end of the batch. This can involve movement through a very wide operating range, and non-linearity in the system can be strong. Batch optimization focuses on maximizing the performance objective by finding the corresponding input variable and state variable trajectories. Since batch production is usually of low volume, high value production, optimization of its operation is critical to make the process viable.

The most common type of process for acid gas removal is the batch-type process, and many involve a chemical process in which the acid gas reacts chemically with the cleaning agent, usually a metal oxide. These processes are not merely physical separation processes in which the acid gas is removed by a physical phenomenon, such as adsorption. Thus, the batch-type processes have the common requirement that the process be operated as a batch system where, at the end of the cycle, the chemical agent must be changed or regenerated in order to continue treating.

Batch processes are limited to removing small amounts of sulfur from fuels, especially when the flow rates of the gas streams and/or there are small concentrations of hydrogen sulfide. These processes include (i) the iron sponge process, (ii) the ChemSweet process, (iii) the SulphaCheck process, (iv) the SulphaTreat process, (v) the zinc oxide process, and (vi) the molecular sieve process.

Baumé Gravity

Baumé gravity is a unit of measurement of specific gravity used in the chemical industry for aqueous caustic soda and aqueous acid. Two arbitrary scales are employed, one for liquids lighter than water and the other for liquids heavier than water. This scale is also used to describe the density of acid solutions (Table B-2).

Table B-2 Explanation of the baumé gravity scale.

For liquids heavier (More dense) than water	For liquids lighter (less dense) than water
0° Bé is the distance the hydrometer sinks in pure water.	0° Bé is the distance the hydrometer sinks in a solution that is 10% w/w sodium chloride (salt, NaCl)
15° Bé is distance the hydrometer sinks in a solution that is 15% w/w sodium chloride (salt, NaCl)	10° Bé is the distance the hydrometer sinks in ° pure water.
To convert from °Bé to specific gravity at 60 F: specific gravity = $145/(145 - ^\circ\text{Bé})$	To convert from Bé to specific gravity at 60 F: specific gravity = $140/(130 + ^\circ\text{Bé})$

Before standardization using specific gravity at the time of World War II, the Baumé scale was generally used in industrial chemistry and pharmacology for the measurement of density of liquids. Currently, the Baumé scale is still used in various industries such as sugar beet processing and in the starch industry and the density of liquid product produced from these two sources could well be presented in degrees Baumé.

Bauxite

Bauxite is an amorphous sedimentary rock that is the chief commercial ore of aluminum. It consists largely of hydrated alumina with variable proportions of iron oxides. In addition, bauxite is the main source of aluminum and gallium. The ore consists mostly of the aluminum minerals gibbsite [$\text{Al}(\text{OH})_3$], boehmite [$\gamma\text{-AlO}(\text{OH})$], and diaspore [$\alpha\text{-AlO}(\text{OH})$] that are mixed with the two iron oxides: goethite [$\text{FeO}(\text{OH})$] and hematite (Fe_2O_3) as well as the aluminum clay minerals kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})$] and small amounts of anatase (TiO_2), and ilmenite (FeTiO_3 or $\text{FeO} \cdot \text{TiO}_2$).

The principal aluminum hydroxide minerals found in varying proportions with bauxites are gibbsite and the polymorphs boehmite and diaspore. Bauxite ores are typically classified according to their intended commercial applications such as an abrasive, a cement constituent, an industrial chemical, and a refractory material. The bulk of world bauxite production (approximately 85%) is used as feed for the manufacture of alumina (Al_2O_3) via a wet chemical caustic leach method (the Bayer process). Subsequently, the majority of the resulting alumina produced from this refining process is in turn employed as the feedstock for the production of aluminum metal by the electrolytic reduction of alumina in a molten bath of natural or synthetic cryolite (Na_3AlF_6).

Bauxite is useful in the alternate energy industry insofar as it can be used as a catalyst to convert many different sulfur compounds, in particular mercaptan derivatives (RSH), into hydrogen sulfide (H_2S), which is subsequently removed by a lye treatment (caustic treatment, alkali treatment).

To prepare aluminum oxide, bauxite is heated in pressure vessels with sodium hydroxide solution at 150–200°C through which aluminum is dissolved as aluminate (Bayer process). After separation of ferruginous residue (red mud) by filtering, pure gibbsite is precipitated when the liquor is cooled and seeded with fine-grained aluminum hydroxide. Gibbsite is converted into aluminum oxide by heating. This is molten at approx. 1,000°C (1,830°F) by addition of cryolite as a flux and reduced to metallic aluminum by a highly energy-consuming electrolytic process (Hall-Héroult process).

During the processing of bauxite to alumina (Al_2O_3) in the Bayer process, gallium accumulates in the sodium hydroxide liquor from which it can be extracted by a variety of methods. Achievable extraction efficiencies critically depend on the original concentration in the bauxite feedstock.

Bauxite ores are industrially important for the supply of aluminum metal, and these ores represent the only raw material used in the production of alumina on a commercial scale. Gallium is a common by-product of the process, and both aluminum and gallium may also be considered as a possible future resource for rare earth elements that find use in renewable energy technologies.

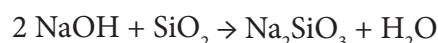
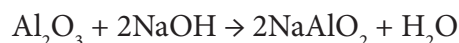
See also: Bauxite Treating Process.

Bauxite Treating Process

Bauxite ore is a mixture of hydrated aluminum oxide derivatives and compounds of other elements such as iron. The aluminum compounds in the bauxite may be present as gibbsite [$\text{Al}(\text{OH})_3$], boehmite [or böhmite, $\gamma\text{-AlO}(\text{OH})$], or diasporite [$\alpha\text{-AlO}(\text{OH})$]. The different forms of the aluminum component and the impurities dictate the extraction conditions. Aluminum oxides and hydroxides are amphoteric – having both acidic and basic character.

In the Bayer process, a mixture of the bauxite ore and a sodium hydroxide solution is heated in a pressure vessel at a temperature of 150 to 200°C (300 to 390°F), causing the aluminum to be dissolved as sodium aluminate. After separation of the residue by filtering, gibbsite is precipitated when the liquid is cooled and then seeded with fine-grained aluminum hydroxide crystals from previous extractions.

The extraction process converts the aluminum oxide in the ore to soluble sodium aluminate (NaAlO_2), and at the same time, silica is dissolved to form sodium silicate (Na_2SiO_3):



The other components of the bauxite ore do not dissolve.

Lime may be added to precipitate the silica as calcium silicate (CaSiO_3). The undissolved waste (bauxite tailings) after the aluminum compounds are extracted contains iron oxides, silica, lime (CaO), titania (TiO_2), and some unreacted alumina.

See also: Bauxite.

Beavon Process

The Beavon sulfur removal process for the cleanup of Claus plant tail gas is a two-step process in which the sulfur contaminants are first catalytically hydrolyzed and/or hydrogenated to hydrogen sulfide and the hydrogen sulfide is then converted to elemental sulfur and recovered in a Stretford process unit.

In the process, which consists of two stages, the sulfur-containing compounds, such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbonyl sulfide (COS), and carbon disulfide (CS_2), are converted to sulfur in over 99.9% efficiency. In the first stage, the various sulfur compounds are either hydrogenated or hydrolyzed to give hydrogen sulfide, while in the second stage, the hydrogen sulfide is oxidized using the Stretford process to give good-quality elemental sulfur. This process can also be utilized in synthetic natural gas plants, natural gas processing, and other similar applications.

See also: Gas Cleaning, Gas Processing, Gas Treating, Tail Gas Cleaning, Wellman-Lord Process.

Benchmark Crude Oil

A benchmark crude oil is a crude oil that is used as the standard crude oil against which the properties of the (liquid) source of any fuel (even a renewable fuel) can be measured or compared. When evaluating the price of any crude oil, it is important to compare the crude oil against an appropriate benchmark crude oil.

The price of crude oil means the spot price of either West Texas Intermediate crude oil as traded on the New York Mercantile Exchange (NYMEX) for delivery in Cushing, Oklahoma, or of Brent crude as traded on the Intercontinental Exchange (ICE, into which the International Petroleum Exchange has been incorporated) for delivery at Sullom Voe. The price of a barrel of oil is highly dependent on both its grade, determined by factors such as its specific gravity or API gravity and sulfur content, as well as location. The vast majority of oil is not traded on an exchange but on an over-the-counter basis, typically with reference to a marker crude oil grade that is typically quoted via pricing. Other important benchmark crude oils include Dubai, Tapis, and the OPEC basket.

For the purposes of pricing, crude oil is generally classified based on the API gravity and sulfur content. For example, light crude oil has low density, low viscosity (there are no exact numbers assigned to this, because the classification is more practical and theoretical), and low sulfur content, making it easier to transport and refine and, therefore, more expensive to purchase. Sweet crude oil has a sulfur content less than 0.5% by weight and is usually (but not always) light crude oil, making it much easier to refine in a way that would meet environmental standards in developed countries - and making it more expensive.

A light crude oil is generally one with an API gravity of less than approximately 40 – for example, Brent crude oil has an API gravity on the order of 38 to 39°. Sweet crude is preferable to sour crude oil because it is also (like light crude) more suited to the production of the most valuable refined products. On the other hand, heavy crude oil has high density, high viscosity, and high sulfur content making it more difficult to transport and refine and cheaper to purchase. Typically, sour crude oil has a sulfur content above 0.5% by weight and is usually *heavy crude oil*, making it cheaper to purchase but more expensive to refine.

Heavy crude oil will typically have an API gravity of 20 or less - the higher the API gravity, the lower the density. Heavy crude oil is harder to handle (it is too thick to pump easily through pipelines unless diluted with light crude) and is more expensive to refine to produce the most valuable crude oil products such as naphtha (gasoline), kerosene, diesel fuel, and aviation fuel.

Because there are so many different varieties and grades of crude oil, buyers and sellers have found it easier to refer to a limited number of reference, or benchmark, crude oils. Other varieties are then priced at a discount or premium, according to their quality. Thus, crude oil is priced in terms of regional blends, each with different characteristics. Of these, certain blends are followed by traders, as they most reflect the overall value of oil, and therefore affect the way different blends are priced. These are essentially like a Consumer Price Index for different types of oil. Approximately 160 different types of crude are traded around the world; the four primary benchmarks, of which these are priced internationally are (i) Brent blend crude oil, (ii) West Texas intermediate (WTI) crude oil, (iii) Dubai crude oil, and (iv) the OPEC Basket crude oil.

The Brent crude oil blend is based on the prices of Brent crude, which is a light, sweet crude oil and is actually a combination of crude oil from 15 different oil fields in the Brent and Ninian systems located in the North Sea. The API gravity is 38.3° (making it a “light” crude oil, but not quite as “light” as West Texas Intermediate crude oil), while it contains approximately 0.37% by weight sulfur (making it a *sweet* crude oil, but again slightly less *sweet* than West Texas Intermediate crude oil). The Brent blend is ideal for making gasoline and middle distillates, both of which are consumed in large quantities in Northwest Europe, where Brent blend crude oil is typically refined. However, if the arbitrage between Brent and other crude oils, including WTI, is favorable for export, Brent has been known to be refined in the United States (typically the East Coast or the Gulf Coast) or the Mediterranean region. Brent blend, like West Texas Intermediate crude oil, production is also on the decline, but it remains the major benchmark for other crude oils in Europe or Africa.

Beta Decay

Beta decay (β -decay) is a type of radioactive in which a beta particle (a fast energetic electron or positron) is emitted from an atomic nucleus which transforms the original nuclide to an isobar of that nuclide.

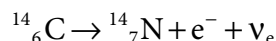
By definition, an isobar is an atom (nuclide) of different chemical elements that have the same number of nucleons. Correspondingly, an isobar differs in atomic number (or the number of protons) but has the same mass number. An example of a series of isobars is ^{40}S , ^{40}Cl , ^{40}Ar , ^{40}K , and ^{40}Ca .

Thus, the beta decay of a neutron transforms it into a proton by the emission of an electron accompanied by an antineutrino or, conversely, a proton is converted into a neutron by the emission of a positron with a neutrino in the positron emission reaction. Neither the beta particle nor its associated (anti-)neutrino exist within the nucleus prior to beta decay, but are created in the decay process. By this process, unstable atoms obtain a more stable ratio of protons to neutrons. The probability of a nuclide decaying due to beta and other forms of decay is determined by the nuclear binding energy.

Thus, the two types of beta decay are known as *beta minus* and *beta plus*. In the former [beta minus decay (β^- decay)], a neutron is converted to a proton, and the process creates an electron and an electron antineutrino, while

in beta plus decay (β^+ decay, also known as positron emission), a proton is converted to a neutron and the process creates a positron and an electron neutrino.

An example of electron emission (β^- decay) is the decay of carbon-14 (^{14}C) into nitrogen-14 (^{14}N) with a half-life on the order of 5,730 years:

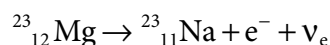


In this form of decay, the original element becomes a new chemical element (nuclear transmutation) and the new element has an unchanged mass number (A) but atomic number (Z) that is increased by one. As in all nuclear decays, the decaying element (in this case $^{14}_6\text{C}$) is the *parent nuclide*, while the resulting element (in this case $^{14}_7\text{N}$) is known as the *daughter nuclide*.

Another example is the decay of hydrogen-3 (^3H , tritium) into helium-3 (^3He) with a half-life on the order of 12.3 years:



An example of positron emission (β^+ decay) is the decay of magnesium-23 (^{23}Mg) into sodium-23 (^{23}Na) with a half-life on the order of 11.3 seconds:



Beta+ decay (β^+ decay) also results in nuclear transmutation, with the resulting element having an atomic number that is decreased by one.

See also: Alpha Decay, Alpha Particle, Nuclear Energy.

Beta Particle

A beta particle is emitted from the nucleus of a radioactive atom with a wide range of energies up to some maximum value. When a beta particle is emitted that is below the maximum value, the neutrino carries away the rest of the energy.

Like the alpha particles, beta particles, like alpha particles, lose energy by ionization and excitation, but because of their small mass (1/7,300 of an alpha particle) and lower charge (1/2 of that of an alpha particle), the interactions take place at less frequent intervals. Therefore, the beta particles do not produce as many ion pairs per centimeter of path as alpha particles, and thus, have a greater range in matter which depends on the energy of the particle and the composition of the material.

See also: Alpha Decay, Alpha Particle, Nuclear Energy.

Bioalcohol

Biologically produced alcohols, such as ethanol, propanol and butanol, are produced by the action of microorganisms and enzymes through the fermentation of starches, sugars, or cellulose. Alcohol fuels are produced by fermentation of sugars derived from corn, molasses, sugar beets, sugar cane, wheat, as well as potato and fruit waste.

However, as an example, there is no difference in properties between ethyl alcohol produced in a petrochemical facility and ethanol from biomass; it is merely the use of the prefix “bio” to define the origin of the alcohol. However, in some cases, ethanol ($\text{C}_2\text{H}_5\text{OH}$) that is derived from crude oil should not be considered safe for consumption as this alcohol contains approximately 5% v/v methanol (CH_3OH) and may cause blindness or death. This mixture may also not be purified by simple distillation, as it forms an azeotropic mixture.

Bioalcohols are a useful type of liquid fuel because they combust rapidly and are often cheap to produce. However, their acceptance is hampered by the fact that their production often requires as much or even more fossil fuel than they replaced since they are typically not primary sources of energy; however, they are a convenient way to store the energy for transportation.

Biomethanol

Methanol (the simplest alcohol, CH_3OH) is the lowest molecular weight and simplest alcohol, produced from natural gas (methane). It is also called methyl alcohol or wood alcohol, the latter because it was formerly produced from the distillation of wood. Currently, the majority of the methanol produced is manufactured from natural gas, a non-renewable fossil fuel, and modern methanol is also produced in a catalytic industrial process directly from carbon monoxide, carbon dioxide, and hydrogen. However, methanol can also be produced from biomass (as biomethanol) using similar chemical processes.

Bioethanol

Ethanol, also known as grain alcohol or ethyl alcohol, is most commonly used in alcoholic beverages. The ethanol production methods used are enzyme digestion (to release sugars from stored starches), fermentation of the sugars, distillation, and drying. Ethanol is produced mostly from carbohydrates produced in starch and sugar crops such as corn or sugar cane. The distillation process requires significant energy input for heat (often unsustainable natural gas, but cellulosic biomass such as bagasse, the waste left after sugar cane is pressed to extract its juice, can also be used more sustainably). Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions.

Two types of grain ethanol production are currently available in the United States, dry milling and wet milling, with the latter predominating among large-scale producers.

Corn dry milling is the most common type of ethanol production in the United States. In the dry grind process, the entire corn kernel is first ground into flour and the starch in the flour is converted to ethanol via fermentation. The other products are carbon dioxide (used in the carbonated beverage industry) and an animal feed called distillers' dried grain with soluble matter.

Corn wet milling is the process of separating the corn kernel into starch, protein, germ, and fiber in an aqueous medium prior to fermentation. The primary products of wet milling include starch and starch-derived products (e.g., high fructose corn syrup and ethanol), corn oil, and corn gluten.

Ethanol can also be produced from other forms of biomass that do not fall under the nomenclature of food crops. One set of production processes is applicable to what is known as cellulosic biomass, including fast-growing fuel crops, agricultural waste such as bagasse and corn stover, and forest and wood processing waste, while a second set of techniques can make use of practically any form of inexpensive biomass including the cellulosic sort as well as the black liquor produced by paper mills, animal wastes, and some types of landfill wastes.

Ethanol can be readily produced by fermentation of simple sugars that are converted from starch crops. Feedstocks for such fermentation ethanol include corn, barley, potato, rice, and wheat. This type of ethanol may be called grain ethanol, whereas ethanol produced from cellulose biomass such as trees and grasses is called bioethanol or biomass ethanol." Both grain ethanol and bioethanol are produced via biochemical processes, while chemical ethanol is synthesized by chemical synthesis routes that do not involve fermentation.

Cellulosic biofuels, such as cellulosic ethanol, began to be produced in commercial-scale plants in 2013. These fuels are made from cellulose-containing organic material. Cellulose forms the primary structural component of green plants and is by far the most abundant organic (carbon-containing) compound on Earth. The primary cell wall of green plants is made primarily of cellulose; the secondary wall contains cellulose with variable amounts of lignin. Lignin and cellulose, considered together, are termed lignocellulose, which (as wood) is the most common biopolymer on Earth. Cellulosic biomass, derived from non-food sources, such as trees and grasses, is also being developed as a feedstock for ethanol production. Even dry ethanol has roughly one-third lower energy content per unit of volume compared to gasoline, so larger (and therefore heavier) fuel tanks are required to travel the same distance, or more fuel stops are required.

Ethanol may also be used as a fuel, most often in combination with gasoline. For the most part, it is used in a 9:1 ratio of gasoline to ethanol to reduce the negative environmental effects of gasoline. There is increasing interest in the

use of a blend of 85% fuel ethanol blended with 15% gasoline. This fuel blend, called E85, has a higher fuel octane than premium gasoline, allowing in properly optimized engine increases in both power and fuel economy over gasoline.

Biopropanol

Propanol (propyl alcohol, C_3H_7OH) is the next member of the alcohol series followed by butanol (butyl alcohol, C_4H_9OH). Both alcohols may be used as a fuel with the normal combustion engine. The advantages of propanol and butanol are the high octane rating (over 100) and high energy content, only approximately 10% lower than gasoline, and subsequently more energy-dense than methanol and ethanol. The major disadvantage of propanol and butanol as fuels for the internal combustion engine is the relative high flashpoint of these alcohols.

Biobutanol

Butanol can be produced from biomass (as biobutanol) as well as fossil fuels, but biobutanol and crude oil-derived butanol (sometimes referred to as petro-butanol) have the same chemical properties. Butanol may be used as a fuel in an internal combustion engine. Because its longer hydrocarbon chain causes it to be fairly non-polar, it is more similar to gasoline than it is to ethanol. Butanol has been demonstrated to work in vehicles designed for use with gasoline without modification, and is thus often claimed to provide a direct replacement for gasoline (in a similar way to biodiesel in diesel engines). Biobutanol has the advantage in combustion engines in that its energy density is closer to gasoline than the simpler alcohols (while still retaining over 25% higher octane rating); however, biobutanol is currently more difficult to produce than ethanol or methanol.

See also: Biodiesel, Biofuels, Biogas, Vegetable Oil.

Biocatalysts

A biocatalyst is a catalyst (such as, for example, an enzyme) that is of biological origin. Thus, biocatalysis is the use of natural catalysts, such as protein enzymes, to perform chemical transformations on organic compounds. Both enzymes that have been more or less isolated and enzymes still residing inside living cells are employed for this task. More than one hundred years ago, biocatalysis was employed to achieve chemical transformations on non-natural man-made organic compounds, and the last 30 years have seen a substantial increase in the application of biocatalysis to produce fine chemicals, especially for the pharmaceutical industry.

Biocatalysts are living (biological) systems that increase the rate of chemical reactions. In biocatalytic processes, natural catalysts, such as enzymes, perform chemical transformations of organic compounds. In fact, enzymes that have been isolated as separate molecular entities as well as enzymes still remain inside living cells are employed as catalysts that can catalyze novel small molecule transformations that may be difficult or impossible using classical synthetic organic chemistry. In addition, enzymes are environmentally benign insofar as they can be completely degraded in the environment.

Biocatalysts do not operate by different scientific principles from organic catalysts. The existence of a multitude of enzyme models including oligopeptide or polypeptide catalysts proves that all enzyme action can be explained by rational chemical and physical principles. However, enzymes can create unusual and superior reaction conditions such as extremely low pK_a values or a high positive potential for a redox metal ion. Enzymes have increasingly been found to catalyze almost any reaction of organic chemistry. Moreover, the notion that biocatalysts are slow catalysts is false and optimized syntheses not only produce high selectivity or total turnover numbers but also satisfactory-to-high yields of products.

See also: Enzymes.

Biochar

Biochar is organic matter that has undergone combustion under low to no oxygen conditions (such as during pyrolysis) resulting in a recalcitrant, high carbon material specifically for use as a soil amendment. Recently, fervent interest in the production of biochar to address issues of fertility, water-holding capacity, remediation, climate change mitigation, etc., led to a much greater understanding of the complexities of this potential amendment in altering soil

biological, chemical, and physical properties. Rather than assume the benefit of any biochar created from any feedstock added to any soil ecosystem, concepts of matching appropriate feedstock and pyrolysis condition to soil type to achieve specific goals associated with remediation, increasing yields, decreasing greenhouse gas emission, and/or climate change mitigation emerged.

This porous sponge-like property of biochar makes it useful for many things such as the production of activated carbon filters used to purify water. Industrial production of biochar employs pyrolysis, a means of combustion without much air or oxygen and that is more efficient in that it produces little ash.

The production of biochar is a sustainable option for waste management since the char contains 50% of the original carbon which is highly recalcitrant in nature; therefore, its production helps in carbon sequestration by locking the carbon present in the plant biomass. The elemental composition and structural configuration of biochar is strongly correlated with temperature, heating rate, and residence time maintained during its production. Along with the biochar, some amount of bio-oil and gases are also produced which can be used for generation of energy and various chemicals.

Soil pH and electrical conductivity (EC) increase in soil incorporated with biochar which may be due to the presence of ash residue that is dominated by carbonates of alkali and alkaline earth metals, and some amount of silica, heavy metals, and organic and inorganic nitrogen. With its large surface area, biochar helps in increasing water holding capacity, cation exchange capacity (CEC), and microbial activity (act as its habitat) and also reduces leaching of nutrient by providing nutrient binding sites. This reduces the total fertilizer requirement of biochar-amended soil and thereby reduces environmental pollution caused by leaching of inorganic fertilizer. It also plays a vital role in increasing crop productivity. Apart from improving soil quality, biochar provides various other benefits such as (i) mitigation of greenhouse gases (such as methane, CH_4 , nitrous oxide, N_2O , and carbon dioxide, CO_2), (ii) a decrease in the dissipation rate of herbicide in soil, and (iii) wastewater treatment. Due to large availability of biomass resources, biochar can be a prime product in many countries.

See also: Pyrolysis.

Biochemical Conversion

Biochemical conversion is the use of (i) fermentation or (ii) anaerobic digestion to produce fuels and chemicals from organic sources. In the general sense, fermentation refers to any chemical change of organic material that is accompanied by effervescence, normally without the participation of oxygen. The important differences between fermentation and anaerobic digestion are the nature of the product produced and the character of the biological contribution. Fermentation produces a liquid product in the presence of enzymes, while anaerobic digestion yields a gaseous product as a result of the metabolic activity of bacteria (Table B-3).

Ethanol is the principal product of the fermentation processes appropriate to biomass conversion, although other alcohols, as well as organic acids, ketones, and aldehydes, may be produced either as main products or as by-products. Anaerobic digestion is the decomposition of any organic material by the metabolic action of bacteria without the participation of atmospheric oxygen. Methane and carbon dioxide are the main products of the decomposition. The source of the oxygen in the carbon dioxide is the combined oxygen in the organic molecules and in the water.

Table B-3 Biomass conversion processes.

Process	Biomass feedstock	Scale*	Product
Combustion	Wood, municipal solid waste, grasses, crop residue	Small, large	Heat, steam, electricity
Gasification	Wood, municipal solid waste (grasses, crop residue)	Large	Low-heat content gas, synthesis gas ethanol
Pyrolysis	Wood, sewage sludge	Large	Medium-heat content gas tar
Fermentation	Grain and sugar crops	Small, large	Ethanol

*Small implies domestic or farm application; large is industrial-scale processing of up to 1,000 t/d of biomass.

Bacterial digestion is in effect accomplished by enzymes. Further, certain bacteria produce acids and alcohols as the principal degradation products. In some cases, it is not clear whether the degradation proceeds as a result of bacterial metabolism, or whether it can be achieved by non-growing cells. Nevertheless, the distinction between the two processes is convenient for presentation purposes, and should not cause confusion in classifying the important biochemical processes currently in contention.

Biomass fermentation to produce ethanol is similar to glycolysis (the fermentation that occurs in muscle tissue and converts glucose to lactic acid with the release of energy), but the use of different enzymes results in different end products.

See also: Aerobic Digestion, Anaerobic Digestion, Bioconversion, Fermentation.

Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) is a chemical procedure for determining the rate of uptake of dissolved oxygen by the rate biological organisms in a body of water use up oxygen. It is a chemical measure of the power of an effluent to deoxygenate water. The test is widely used as an indication of the quality of water. The biochemical oxygen demand can be used as a gauge of the effectiveness of wastewater treatment plants. There are two recognized methods for the measurement of biochemical oxygen demand which are (i) the dilution method and (ii) the manometric method.

In the dilution method, a small amount of microorganism seed is added to each sample being tested. This seed is typically generated by diluting activated sludge with de-ionized water. The test is carried out by diluting the sample with oxygen saturated de-ionized water, inoculating it with a fixed aliquot of seed, measuring the dissolved oxygen, and then sealing the sample to prevent further oxygen dissolving in. The sample is kept at 20°C in the dark to prevent photosynthesis (and thereby the addition of oxygen) for five days, and the dissolved oxygen is measured again. The difference between the final dissolved oxygen and initial dissolved oxygen is the biochemical oxygen demand. The apparent biochemical oxygen demand for the control is subtracted from the control result to provide the corrected value.

In the manometric method, the sample is kept in a sealed container fitted with a pressure sensor. A substance that absorbs carbon dioxide (typically lithium hydroxide) is added in the container above the sample level. The sample is stored in conditions identical to the dilution method. Oxygen is consumed, and dioxide is released. The total amount of gas, and thus the pressure, decreases because carbon dioxide is absorbed. From the drop of pressure, the sensor electronics computes and displays the consumed quantity of oxygen.

Biochemicals

Biochemicals, as opposed to petrochemicals, are in the context of this encyclopedia, chemicals produced from biomass.

The production of chemicals from biomass, a renewable feedstock, is highly desirable in replacing petrochemicals to make biorefineries more economical. The best approach to compete with fossil-based refineries is the upgradation of biomass in integrated biorefineries. The integrated biorefineries employed various biomass feedstocks and conversion technologies to produce biofuels and bio-based chemicals. Bio-based chemicals can help to replace a large fraction of industrial chemicals and materials from fossil resources. Biomass-derived chemicals, such as 5-hydroxymethylfurfural (5-HMF), levulinic acid, furfurals, sugar alcohols, lactic acid, succinic acid, and phenols, are considered platform chemicals. These platform chemicals can be further used for the production of a variety of important chemicals on an industrial scale. However, current industrial production relies on relatively old and inefficient strategies and low production yields, which have decreased their competitiveness with fossil-based alternatives.

Biomass feedstocks, such as agricultural residues and wood chips, constitute an inexpensive renewable resource for commercial large-scale biorefineries, as these waste products are widely available and can sequester carbon. The target chemicals include alcohol derivatives, organic acid derivatives such as formic acid and levulinic acid, and furan derivatives such as 5-hydroxymethylfurfural (5-HMF) and furfural derivatives. These chemicals can further be converted to a range of derivatives that have potential applications in biofuels, polymers, and solvent industries.

Due to these differences in their chemical composition and structure, cellulose, hemicellulose, and lignin have different chemical reactivities. In addition to the complex nature of bio-resources, the inert chemical structure and compositional ratio of carbon, hydrogen, and oxygen in molecules in biomass present difficulties in the chemo-catalytic conversion of biomass to fuels and chemicals. Therefore, besides using the natural lignocellulosic biomass as a reactant, researchers often use model compounds for conversion process studies. In addition, the development of highly active and selective catalysts for the chemo-selective catalytic conversion of lignocellulosic biomass to desired products remains a daunting challenge.

The development of processes and technologies to convert lignocellulosic biomass to fuels and value-added chemicals remains a significant challenge. In this context, the major difficulty in producing a high yield of target chemicals and fuels is the complex chemical composition of lignocellulosic biomass feedstocks. Structurally, cellulose contains anhydrous glucose units and hemicellulose consists of different C5 sugar monomers. On the other hand, lignin is a complex, three-dimensional, and cross-linked biopolymer having phenylpropane units with relatively hydrophobic and aromatic properties. Due to these differences in their chemical composition and structure, cellulose, hemicellulose, and lignin have different chemical reactivities. In addition to the complex nature of bio-resources, the inert chemical structure and compositional ratio of carbon, hydrogen, and oxygen in molecules in biomass present difficulties in the chemo-catalytic conversion of biomass to fuels and chemicals.

A variety of methods can be employed to obtain different product portfolios of bulk chemicals, fuels, and materials. Biotechnology-based conversion processes can be used to ferment the biomass carbohydrate content into sugars that can then be further processed. For instance, the fermentation path to lactic acid shows promise as a route to bio-degradable plastics and has been demonstrated commercially. An alternative is to employ thermochemical conversion processes which use pyrolysis or gasification of biomass to produce a hydrogen-rich synthesis gas. This synthesis gas can then be used in a wide range of chemical processes.

While the concept of exploiting the wide range of chemicals from plants may appear novel, the published literature shows that large numbers of metabolites have already been identified and characterized from a wide variety of plant species. For example, over 37,000 different potential and unexploited materials can be identified. These have a wide range of chemical, physical, and biological properties and include phenolics, nitrogen containing compounds, and terpenes (terpenoids). The variety of molecular compounds is vast. For example, in the terpene group, there are six sub-groupings of molecules with a large number of applications including use in anti-cancer drugs.

Extraction procedures can have a major impact on the availability of these chemicals, and, to ensure optimal exploitation, some of the well-established extraction procedures may need to be revised. For example, in winter rapeseed, the harvested seed is crushed and rapeseed oil extracted mechanically. The residual meal is then treated with hexane to extract the remaining oil, before being used as feed, primarily for ruminants. Rapeseed oil components have numerous applications including use in bio-diesel, and specialty chemicals.

However, innovative oil-extraction procedures could allow greater exploitation of protein-based metabolites in the rapeseed, which can comprise 25% or more of the rapeseed mass. Research from studies, such as the EC-funded Enhance project, has demonstrated that this separation would allow products to be produced for numerous applications (see diagram) with base cellulose material and some other metabolites remaining in the residual meal.

See also: Biofuels, Petrochemicals.

Biochemicals - Production

Basic knowledge of the mechanisms of common reactions such as dehydration, hydrogenation, and hydrodeoxygenation involved in biomass upgradation processes is discussed in the following section.

Dehydration

Dehydration is a reaction in which a water molecule is removed from the substrate, mainly alcohol, forming an alkene or other unsaturated product depending on the substrate. The reaction is commonly catalyzed by Lewis or Brønsted acids, as the hydroxyl group is a poor leaving group. Dehydration in the presence of a Brønsted acid catalyst occurs by first protonating the hydroxyl group, as the protonated hydroxyl group ($\text{R-H}_2\text{O}^+$) is a better leaving group

than the hydroxyl group. As a result, the catalyst is eliminated as water. Simultaneously, a carbon-carbon double bond ($C=C$) is formed in the carbon skeleton of the substrate, as per Zaitsev's rule.

In Lewis acid-catalyzed reactions, however, the reaction proceeds through the bonding of Lewis acid to the lone electron pair of hydrogen-oxygen. The electrophile nature of the Lewis acid lowers the electron density in the alcohol carbon-oxygen bond, which results in the cleavage of the alcohol carbon-oxygen ($C-O$) bond and the formation of alkene and Lewis acid hydroxide specie. The Lewis acid hydroxide reacts with the released β -proton, forming water and the original catalyst species.

Due to the abundances of hydroxyl groups in a wide variety of natural resources, dehydration reactions are the most common and important ways to valorize biomass. As a result, different dehydration products can be obtained from biomass, and are used as high-value chemicals.

Hydrogenation

Hydrogenation is a reaction in which hydrogen atoms are added to an unsaturated compound to reduce the double and triple bonds. Molecular hydrogen (H_2 , gaseous) and other compounds (transfer hydrogenation) can be used as a hydrogen source in the reaction. However, the addition of hydrogen does not take place without a catalyst; therefore, the reaction is catalyzed by homogeneous and heterogeneous catalysts to increase the feasibility of reactions at the laboratory and industrial scales within short time durations. Most commonly, heterogeneous systems with solid metal hydrogenation catalysts and molecular hydrogen are used as catalysts for biomass conversion reactions.

Hydrogenation with a heterogeneous solid metal catalyst and hydrogen follows the Horiuti-Polanyi mechanism. First, the hydrogen molecule is chemisorbed on the surface of the catalyst, followed by the scission of a hydrogen-hydrogen ($H-H$) bond producing two adsorbed hydrogen atoms. Next, the unsaturated reactant is adsorbed on the catalyst. The opening of a double bond through chemisorption follows this. The hydrogen atoms are transferred to the chemisorbed reactant on the surface of the catalyst in a stepwise manner of which the first hydrogen transfer is reversible. The second hydrogen transfer forms the reduced reaction product, and then it is desorbed from the surface of the catalyst, thus completing the reaction cycle.

Hydrogenation is the most fundamental reaction in chemistry. Nature produces many different unsaturated products including carbon-carbon double ($C=C$) bonds, in carbonyl groups, in the structural aldoses and ketoses of cellulose and hemicellulose. The hydrogenation of these biomass-derived monosaccharides in lignocellulosic biomass produces sugar alcohols. For example, hydrogenation of glucose and xylose, the main components in lignocellulosic biomass, produces sorbitol and xylitol, respectively. In addition, the dehydration products can be further upgraded through hydrogenation. These hydrogenation products can be used as solvents, monomers, and biofuels. The synthesis and uses of hydrogenation of biomass-derived substrates will be covered in more detail.

Hydrodeoxygenation

Hydrodeoxygenation (HDO) is a hydrogenolytic reaction in which the removal of the oxygen atom from the reactant occurs in the presence of hydrogen (H_2). The removal of oxygen-containing functionalities can occur through direct hydrogenolysis ($C-O$ bond cleaved with hydrogen), dehydration ($C-O$ bond cleaved through the removal of water), decarbonylation (removal of carbon monoxide), and decarboxylation (removal of carbon dioxide). The most common hydrodeoxygenation pathways depend on the oxygen moieties. Hydrodeoxygenation also needs selective catalysts to facilitate the formation of the desired reaction products. Catalysts typically contain noble metals as the hydrogenation catalyst, as well as Brønsted or Lewis acidic sites for cleavage of the carbon-oxygen bonds. The hydrodeoxygenation mechanisms of different oxygen functionalities depend on the reaction conditions and catalysts used.

In the case of biomass or biomass-derived substrates, hydrodeoxygenation reactions are used to reduce high oxygen content. Typically, these hydrodeoxygenation reactions require a high temperature and high pressure, possibly resulting in the formation of product mixtures through cleavage of carbon-carbon bonds and carbon skeleton rearrangements. In this context, new catalytic systems need to be developed to remove the oxygen-containing functionalities.

Production from Lignin

Lignin is the key constituent of the lignocellulosic biomass and responsible for the structural and mechanical integrity of plants. Lignin is a polymer with wide variability in structure. Its components depend on the biomass source

and are most often combined with cellulose and hemicelluloses. It is considered the least susceptible to chemical and biotransformation techniques. Therefore, lignin often becomes a low-value waste product of biomass processing technologies, such as in the conventional paper and pulp industry and in the modern bioethanol-fuel-production industry. Therefore, lignin valorization in relation to energy, chemical, and biotechnological application is creating considerable interest to researchers.

Structurally, lignin is a three-dimensional amorphous phenolic polymer that consists of monomers such as phenylpropane unit, C3C6 including p-coumaryl, sinapyl, and coniferyl alcohol. It contains β -O-4 (40% to 60%), biphenyl (3.5% to 25%), α -O-4 (3% to 5%), and β -5 (4% to 10%) linkages. The different structural and chemical properties of lignin lead to the production of a wide variety of aromatic chemicals. Therefore, lignin was observed as the major aromatic source of the bio-based economy. Dimethyl sulfide, vanillin, and dimethyl sulfoxides are the chemicals, manufactured from lignin on a large scale. Several researchers have summarized the applications of lignin as a renewable resource, such as emulsifier, bio-dispersant, polyurethane foams, wood panel products, resins, automotive brakes, and precursors for the synthesis of thermoplastic materials in the industry. In addition, the production of aromatics from depolymerization of lignin is considered as the most promising process for the sustainable utilization of lignin. Aromatics can be derived from monomeric C6 fragments from depolymerized lignin. The maximum theoretical obtainable yield of benzene, toluene, and xylene (BTX) from lignin is approximately 36 to 42%, as lignin contains 60% to 65% carbon in C6 aromatic rings. The main challenge in producing aromatics is to selectively deoxygenate and dealkylate the C6 aromatic structure (typically with hydrogen) without hydrogenating C6 aromatic rings. The difficulty in the valorization of lignin originates from its complex polymeric structure, which differs from one lignin to another depending on the botanical origin and the pretreatment used for its separation from carbohydrates (cellulose and hemicellulose).

The catalytic pathways, including base-catalyzed depolymerization, pyrolysis, and Lewis acid-catalyzed solvolysis, have been investigated and studied for the conversion of lignin to valuable compounds. Low product yields and severe treatment conditions, as well as complex product mixtures, have been major drawbacks for lignin conversion. However, lignin's aromatic nature and its versatile functional groups suggest that it can be a valuable source of chemicals, particularly monomeric phenolics. Hydrothermal liquefaction of lignin in the presence of water as the solvent leads to the production of bulk aromatic compounds. Bio-oil obtained after lignin decomposition contains monomeric phenols and oligomeric polyphenols. The monomeric phenols are valuable chemicals; however, the oligomeric polyphenols that existed in bio-oils were volatile and viscous, which makes them more difficult for conversion into useful products. As a result, the conversion of lignin to monomers instead of oligomers is highly desirable.

The thermochemical conversions such as catalytic fast pyrolysis and microwave pyrolysis were commonly used processes in the presence of effective catalysts to enhance reactions, including cracking, decarbonylation, deoxygenation, and decarboxylation. Recently, several studies have been reported for lignin depolymerization to obtain monomeric phenols. The monomers of phenols such as alkylated phenol and guaiacol have found applications as intermediates for the production of polymers, antioxidants, resins, medicines, and pesticides. The preparation of phenolic resins such as phenol-formaldehyde using phenolic-rich pyrolysis oils is well known.

Phenolic compounds are obtained from lignocellulosic biomass after treatment with alkali. A large number of different methods have been discussed, but the processes reported are complex, low yielding, cost-ineffective, and energy inefficient. The most challenging aspect of the production of chemicals from lignin-derived monomeric phenols using catalytic hydrotreatment is the synthesis of catalysts that can perform deoxygenation without saturating the aromatic rings in the phenol deoxygenation processes. This will help to decrease the hydrogen consumption. For this process, mainly conventional metal sulfide, metal oxide, transition metal phosphide, metal carbides, and bi-metallic catalysts were used. Bi-metallic catalysts are found to be more suitable than monometallic catalysts for deoxygenation of phenols.

Ni-based catalysts were used for lignin hydrogenation/hydrogenolysis in 1940. Ni catalysts supported on carbon and magnesium oxide were found to be active for C-O bond cleavage of model compounds as well as selectively hydrogenating the aryl ether C-O bonds of β -O-4 without disturbing the arenes. The alcohol solvents were used as a hydrogen donor for the hydrogenolysis of lignin. The platinum group metals (palladium, Pd, platinum, Pt, ruthenium, Ru, rhodium, Rh, and iridium, Ir) bear higher intrinsic activity than Ni catalysts and hence were widely reported for hydrogenolysis of lignin. Zn in Pd-based catalysts was found to be far more effective than the Pd/C catalyst and Zn-based catalysts were effective for the cleavage of β -O-4 bonds in lignin model compounds.

Oxidative depolymerization of lignin leads to the production of polyfunctional aromatic compounds. These compounds include aromatic aldehydes and carboxylic acids, such as 4-hydroxybenzaldehyde, vanillin, muconic acid, and syringaldehyde, which are good alternatives to crude oil-based chemicals. The depolymerization of lignin in 1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate with nitrate catalysts yielded pure 2,6-dimethoxy-1,4-benzoquinone. The catalytic systems for lignin oxidation involve organometallic catalysts, metal-free organometallic catalysts, acid or base catalysts, metal salt catalysts, photocatalytic, and electrocatalytic oxidation. Methyltrioxorhenium (MTO) in combination with H_2O_2 catalyzed lignin oxidation reactions is the most promising. This catalytic system leads to extensive oxidation on the aliphatic side-chain and aromatic-ring cleavages.

Lignin-Derived Polymers

After the depolymerization and production of aromatic compounds from lignin, the consequent processes do not require much advancement. The mature technologies already exist for the transformations of aromatic compounds into commodity monomers and polymers. The commodity polymers that can be derived from lignin are polyethylene terephthalate (PET), Kevlar, polystyrene, polyanilines, and unsaturated polyesters. The alternatives to fossil-based aromatic polymers could be accomplished by the full valorization of lignin. The synthesis of bio-based PET can be realized by the preparation of ethylene glycol (EG) and p-terephthalic acid from renewable biomass. Bio-based p-xylene can be used as the raw material for p-terephthalic acid to produce a 100% plant-based PET. Sulfur-free lignin derivatives have been widely used as a raw material for wood panel products, polyurethane foams, automotive brakes, biodispersants, and epoxy resins for printed board circuits. Cornstalk-derived bio-oils were used to synthesize phenol-formaldehyde resins.

An integrated biorefinery approach will optimize the utilization of renewable biomass for the production of bio-energy, biofuels, and bio-derived chemicals for the short- and long-term sustainability. For an integrated biorefinery, the concept of usage of platform intermediates as precursors to different products by chemo-catalytic routes will be of highest importance. This will offer the refinery the necessary adaptability to product demand. This review summarizes the production of platform chemicals from lignocellulosic biomass components. The three main components of lignocellulosic biomass, cellulose, hemicellulose, and lignin are valuable precursors for numerous chemicals having valuable applications. The target chemicals include furan derivatives, such as 5-hydroxymethylfurfural (5-HMF), 2,5-dimethylfuran (2,5-DMF), sugar alcohols and organic acids, such as levulinic acid, lactic acid, succinic acid, and aromatic chemicals. These chemicals can be further converted to a range of derivatives that have potential applications in the polymer and solvent industries. The chemo-catalytic routes were found to be most promising ones for the conversion of biomass feedstocks to these high-value chemicals.

Production from Sugars

Cellulose and hemicellulose are the polymers of C6 and C5 sugar units that are linked by ether bonds. Cellulose consists of D-glucose units connected by β -1-4 linkages and extensive hydrogen bonding which makes the hydrolysis process difficult. Acid and enzymatic hydrolysis are commonly used to liberate the monosaccharide glucose units. Hemicellulose contains C5-sugars, such as xylose, galactose, mannose, and arabinose. The dehydration of C5 sugars can yield furfural, which is a platform chemical that has applications ranging from solvents to resin and fuel additives. The large-scale synthesis of organic chemicals and chemicals based on furan from sugars is an important alternative to crude oil-based energy resources.

Hydroxymethylfurfural

Hydroxymethylfurfural (5-HMF), also 5-(hydroxymethyl)furfural (5-HMF) is the most important platform chemical from renewable feedstock for the next-generation plastic and biofuel production. The derivatives such as levulinic acid, 2,5-bis(hydroxymethyl)furan (2,5-BHF), 2,5-dimethylfuran (2,5-DMF), and 2,5-diformylfuran (2,5-DFF) were synthesized from 5-HMF. Other derivatives are 1,6-hexanediol, 5-hydroxymethyl-2-furan carboxylic acid (HMFCA), 2,5-furfuryldiamine, 2,5-furfuryldiisocyanate, and 5-hydroxymethyl furfuryliden ester. These derivatives have found applications as precursors for the synthesis of materials such as polyesters, polyamides, and polyurethane. The synthesized polymeric materials exhibit good properties. Polyurethane demonstrates high resistance to thermal treatments; photoreactive polyesters have been used for ink formulations, and Kevlar-like polyamides exhibit liquid crystal behavior.

The formation of furan-based derivatives from the hydroxymethylfurfural by catalytic oxidation and hydrogenation processes is reported in Figure 8. The chemicals obtained include 2,5-diformylfuran (2,5-DFF), 2,5-dimethylfuran (2,5-DMF), 2,5-furan dicarboxylic acid (2,5-FDCA), and 2,5-bis(hydroxymethyl)furan (2,5-BHF). 2,5-DFF is produced by the selective and partial oxidation of 5-HMF. It is used in the synthesis of fungicides, drugs, and polymeric materials. Several promising catalytic routes for 2,5-DFF production are reported in the literature. The complete transformation of 5-HMF with a 90% yield of 2,5-DFF was achieved with a vanadium oxide titanium oxide (V_2O_5/TiO_2) catalyst in the presence of air and toluene or methyl isobutyl ketone (MIBK) as the solvent.

Furfural

Furfural is also considered a key chemical produced in lignocellulosic biomass refineries. Hemicellulose, which contains a large amount of C5 sugars xylose and arabinose, can serve as a raw material for the production of furfural. This industrial chemical is mainly obtained from xylose by dehydration. Furfural has been used as a foundry sand linker in the refining of lubricating oil. The use of furfural as an intermediate for the production of chemicals such as furan, furfuryl alcohol, and tetrahydrofuran (THF) has been reported. Reviews have been published on the chemistry of furfural.

Commercially, furfural is produced by the acid-catalyzed transformation of pentosan sugars; C5 polysaccharides are first hydrolyzed by H_2SO_4 to monosaccharides (mainly xylose), which are subsequently dehydrated to furfural. Furfural is then recovered from the liquid phase by steam stripping to avoid further degradation and purified by double distillation. Several reports on the conversion of raw biomass into C5 sugars and furfural using mineral acid and solid acid catalysts were published. The use of these catalysts makes the reaction system more corrosive, which increases the capital costs of the processes. The use of ionic liquids for furfural manufacture has been widely discussed. An ionic liquid plays a role as an acidic catalyst for pentose dehydration in aqueous media, eventually in the presence of organic solvents. These can also act as additives for improving the furfural yields in the reaction media comprised of xylose or xylan, organic solvent, and acidic catalysts. Ionic liquids can also serve as a reaction medium for furfural manufacturing from pentoses, higher saccharides made up of pentoses, or pentosans.

The important chemical obtained from furfural is furfuryl alcohol (FA), and approximately 65% of the overall furfural produced is consumed for the production of FA. FA is currently manufactured industrially by hydrogenation of furfural in the gas or liquid phase over Cu-Cr catalysts. However, chromium in these catalysts causes serious environmental problems because of its high toxicity. Therefore, current studies are focused on exploring more environmentally acceptable catalysts that could selectively hydrogenate the carbonyl group while preserving the C=C bonds. The hydrogenation of furfural over Raney Ni modified by impregnation with heteropolyacid (HPA) salts, such as $Cu_3/2PMo_{12}O_{40}$, that produced a 96.5% yield of furfuryl alcohol was reported. Recently, novel catalyst synthesis methods such as atomic layer deposition (ALD) and encapsulation in metal organic frameworks have been reported.

2-Methylfuran (2-MF) is another industrial chemical that can be synthesized from furfural. 2-MF is also a biofuel component. Another one, tetrahydrofurfuryl alcohol (THFA), is typically produced from furfural via furfuryl alcohol as an intermediate. The hydrogenolysis of tetrahydrofurfuryl alcohol to 1, 5-pentanediol (1, 5-Ped), a promising biofuel component, was disclosed using Rh-MoOx/SiO₂ and Rh-ReOx/SiO₂ catalysts with 85% and 86% yields, respectively. Furfuryl alcohol and THFA are widely used as green solvents for the synthesis of resins. These can also be used as raw materials for the synthesis of fuels and fuel additives. Cyclopentanone (CPO) is another C5 chemical that can be synthesized from furfural. CPO can be widely used in the production of fuels and polymeric materials. Mainly, Cu-based catalysts are used for the transformation of furfural to cyclopentanone.

The decarboxylation of furfural leads to the production of furan. The hydrogenation of furan produced tetrahydrofuran (THF). Furan and THF are also important industrial chemicals. Furfural can be decarboxylated in both gas- and liquid-phase reactions. Supported noble metal catalysts (Pd, Pt, Rh) and mixed metal oxides, such as Zn-Fe, Zn-Cr, Zn-Cr, and Mn were investigated. The decarboxylation has been found to be most efficient with Pd-based catalysts at a high pressure of hydrogen and a high and reaction temperature. These rigorous reaction conditions result in catalyst deactivation. Additionally, the noble metals used are expensive and limited in abundance. Therefore, alternate active and selective catalysts need to be explored.

The oxidation of furfural can also lead to the production of C4 chemicals such as maleic anhydride (MAN), maleic acid (MA), and succinic acid (SA). The use of vanadium oxide-based catalysts has been studied for gas-phase

oxidation of furfural to maleic anhydride with oxygen. The use of oxidants such as oxygen and hydrogen peroxide (H_2O_2) was also discussed for the oxidation of furfural. The combination of copper nitrates with phosphomolybdic acids selectively converts furfural to maleic acid with a 49.2% yield or maleic anhydride with a 54% yield in a liquid medium using oxygen as an oxidant.

Sugar Alcohols

Lignocellulosic-based sugar alcohols, such as sorbitol, mannitol, xylitol, and erythritol, are potential fuels and chemicals widely used for polymer, food, and pharmaceutical applications. These are extensively used as moisturizers, sweeteners, softeners, texturizers, and food for diabetic patients. Currently, sorbitol and mannitol can be synthesized through hydrogenation of fructose and glucose. Xylitol and erythritol can be prepared by the conversion of xylose and glucose, respectively. Many catalytic systems and methods have been reported for the conversion of cellulose into sorbitol and mannitol via hydrolysis followed by hydrogenation. The use of noble metal-based catalysts Pt/SBA-15 and Ru-PTA/MIL-100(Cr) for the conversion of glucose and cellulose into sorbitol, respectively, were reported. However, cheaper non-metal catalysts (supported on TiO_2 , Al_2O_3 , SiO_2 , MgO, ZnO, and ZrO_2) have been found to be effective in converting cellulose into sorbitol and mannitol.

Industrially, xylitol is synthesized by the hydrogenation of pure xylose, while xylose can be obtained through acidic hydrolysis of hemicellulose biomass (corncocks and hardwoods). The first report on the synthesis of xylitol through the hydrogenation of xylose over a Raney Ni catalyst was carried out in a three-phase slurry reactor. The acid-transition metal or bi-functional catalysts were used for the hydrolysis and hydrogenation of cellulose to sugar alcohols in the presence of hydrogen pressure.

Erythritol is a C4-sugar alcohol, mainly found in food ingredients. It occurs as a metabolite or storage compound in fruits, such as grapes, pears, seaweed, and fungi. Pentose sugars (arabinose and xylose) are the precursors for producing C4-sugar alcohols. The most efficient route for the synthesis of erythritol from pentose sugars is selective cleavage of a carbon-carbon bond. The production of erythritol and threitol is mostly carried out at a high temperature range of 200 to 240°C (390 to 465°F) with a pressure of hydrogen pressure of in alkaline conditions. Very few findings relate to the selective bond cleavage to produce erythritol.

Succinic Acid

Succinic acid is one of the 12 high-value bio-based chemicals investigated by Werpy and Peterson as a compound that has the potential to improve the profitability and productivity of biorefineries. Conventionally, succinic acid is produced from maleic acid using Pd/C heterogeneous metal catalysts. Other methods reported for succinic acid production are oxidation of 1,4-butanediol with nitric acid; the carbonylation of ethylene glycol, acetylene, and dioxane; hydrogenation of fumaric acid in the presence of Ru catalyst; and the condensation of acetonitrile to produce butanedinitrile, which can be subsequently hydrolyzed to succinic acid.

Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is an important chemical. It is an alternative for producing alkyl lactates, propylene glycol, propylene oxide, acrylic acid, and poly (lactic acid). Lactic acid has applications in food, pharmaceuticals, and cosmetics. In particular, the biopolymers from lactic acid have created a strong interest. Conventionally, lactic acid is produced via fermentation from carbohydrates.

Lactic acid can be made from different reagents such as lignocellulosic materials, cellulose, carbohydrates, sugars, trioses, glycolaldehyde, and glycerol. The production of lactic acid involves complex reactions of several types of transformations such as aldol condensation, retro-aldol condensation, dehydration, and 1,2-hydride shifts.

Several homogeneous and heterogeneous catalysts have been reported for the production of lactic acid from biomass. The catalysts such as alkali metal ions, tin chloride, tin dioxide (SnO_2), acidic resins, zeolites, metal-modified zeolites, mesoporous materials, tungstated alumina, mixed-oxides, and carbon-silica hybrid materials have been reported in the literature. The use of Rh/C, Ru/C, Ir/C, Ir/ CaCO_3 , and Pt/C catalysts for the transformation of glycerol to lactic acid was discussed. Typically, the highest yield of lactic acid has been achieved in the presence of an inert gas and alkaline medium (CaCO_3). An alkaline platinum-calcium carbonate (Pt/CaCO_3) catalyst has been shown to be an efficient catalyst for glycerol transformation to lactic acid, with 54% selectivity for lactic acid at 45%

conversion in the presence of borate esters at 200°C (390°F). The Rh/Al₂O₃ catalyst also gives high selectivity for lactic acid, i.e., 69% in the presence of borate derivatives.

Chemicals such as pyruvic acid, acrylic acid, 2,3-pentanedione, polylactic acid (PLA), lactic acid esters, and 1,2-propanediol (1,2-PDO) can be synthesized from lactic acid. The polylactic acid can be synthesized by two ways: direct polycondensation of LA and ring-opening polymerization of the lactide monomer (cyclic). The direct polycondensation of lactic acid is a difficult process because of the strong equilibrium between polylactic acid, water, and lactide that limits the synthesis of high molecular weight products. The most commonly used process is using the lactide intermediate. The lactide intermediate was polymerized via a homogeneously catalyzed ring-opening polymerization (absence of water), which produces two lactoyl units in the growing chain. This process suffers from racemization. Consequently, when commercial L-lactic acid was used, a 5% to 12% yield of undesired product (meso-lactide) was produced. The properties of polylactic acid depend mainly on the stereo-composition of the feed used. Therefore, stereo-pure L,L-lactide is used to obtain stereo-pure poly-L-lactic acid. As a result, improvements in catalysts, process parameters, and configuration have been reported.

Catalytic dehydration of lactic acid leads to acrylic acid, while propanoic and pyruvic acids were obtained by lactic acid reduction and dehydrogenation, respectively. 2,3-pentanedione can be produced by condensation and acetaldehyde by either decarbonylation or decarboxylation. The lactic acid conversion to acetaldehyde was investigated on silica-supported heteropolyacid with an 83% yield.

Hydrogenation of lactic acid to 1,2-propanediol was performed in both the liquid as well as the vapor phase using Ru/C and Cu/SiO₂ catalysts, respectively. The direct hydrogenolysis of lactic acid seems an attractive option, but deactivation of catalyst makes the process undesirable. The catalyst deactivation occurs as a result of the polymerization of lactic acid and formation of the side-products, propionic acid. Therefore, to avoid this problem, carboxylic acids are usually converted into more readily reducible esters.

In summary, the catalytic conversions of sugars to commodity chemicals are widely discussed, but the industrial applications are limited. Therefore, further research for the improvements of the catalytic conversion and selectivity are still required for achieving the goal of integrated biorefineries. The areas that need attention are the search for novel reaction media to use efficient catalysts for the biomass conversion processes and the extraction/purification steps to isolate the chemicals with high yield and purity.

See also: Biochemicals, Carbohydrates, Coniferyl Alcohol, p-Coumaryl Alcohol, Lignin, Sinapyl Alcohol, Sugars and Starch.

Bioconversion

Bioconversion is the use of biological agents to carry out a structured deconstruction of lignocellulose components. This platform combines process elements of pretreatment with enzymatic hydrolysis to release carbohydrates and lignin from wood.

The first step is a pretreatment stage which is based on existing pulping processes; however, traditional pulping parameters are defined by resulting paper properties and desired yields, while optimum bioconversion pretreatment is defined by the accessibility of the resulting pulp to enzymatic hydrolysis. This function of this step is to optimize the biomass feedstock for further processing and is designed to expose cellulose and hemicellulose for subsequent enzymatic hydrolysis, increasing the surface area of the substrate for enzymatic action to take place. The lignin is either softened or removed, and individual cellulosic fibers are released creating pulp.

In order to improve the ability of the pretreatment stage to optimize biomass for enzymatic hydrolysis, a number of non-traditional pulping techniques have been suggested and include (i) water-based systems, such as steam-explosion pulping, (ii) acid treatment using concentrated or dilute sulfuric acid, (iii) alkali treatment using recirculated ammonia, and (iv) organic solvent pulping systems using acetic acid or ethanol. As with traditional pulping, pretreatment tends to work best with a homogenous batch of wood chips, but the pretreatment option may have to be selected according to the type of lignocellulosic feedstock.

Once pretreated, the cellulose and hemicellulose components of wood can be hydrolyzed (in this option) using enzymes to facilitate bioconversion of the wood. Enzymatic hydrolysis of lignocellulose materials uses cellulase enzymes to break down the cellulosic microfibril structure into the various carbohydrate components.

The enzymatic hydrolysis step may be completely separate from the other stages of the bioconversion process, or it may be combined with the fermentation of carbohydrate intermediates to end-products. Separate hydrolysis and fermentation (SHF) stages may offer this option more flexibility insofar as process adaptation to feedstock type and product slate is available. Simultaneous saccharification and fermentation (SSF) have been found to be highly effective in the production of specific end products, such as bioethanol.

The benefit of bioconversion is that it provides a range of intermediate products, including glucose, galactose, mannose, xylose, and arabinose, which can be relatively easily processed into value-added bioproducts. The process also generates a quantity of lignin or lignin components; depending upon the pretreatment, lignin components may be found in the hydrolysate after enzymatic hydrolysis, or in the wash from the pretreatment stage. The chemical characteristics of the lignin are therefore heavily influenced by the type of pretreatment that is employed. Finally, a relatively small amount of extractives may be retrieved from the process. These extractives are highly variable depending upon the feedstock employed, but may include resins, terpenes, or fatty acids.

Once hydrolyzed, six-carbon sugars can be fermented to ethanol using yeast-based processes. Five-carbon sugars, however, are more difficult to ferment and lack the efficiency of six-carbon sugar conversion. Bacterial fermentation under aerobic and anaerobic conditions is also an option to expand the variety of other products.

A large number of options on the various aspects of bioconversion are available. The environmental performance of bioethanol, including air quality (NO_x, PM, SO_x, etc.) is also well documented as are the mass-balance and energy-balance of the bioconversion process and economic analyses.

See also: Biochemical Conversion.

Bioconversion Platform

The bioconversion platform is an industrial option (as might be used in a biorefinery) for producing fuels from biomass using biochemical reactions and/or biochemical agents. For example, fermentation or anaerobic digestion to produce fuels and chemicals from organic sources is a bioconversion platform. The bioconversion platform therefore has the ability to serve as the basis for wood-based biorefining operations, generating value-added bioproducts as well as fuel and energy for the forest sector.

The bioconversion platform typically uses a combination of physical or chemical pretreatment and enzymatic hydrolysis to convert lignocellulose into its component monomers. Once liberated, the carbohydrate components of wood may be processed into a number of chemical and fuel products.

Bioconversion technology is leading the way to new chemical products from the lignocellulose-based biorefinery, including bioethanol, lactic acid and polylactide, propanediol, and succinic acid. Other chemical products can be used to create consumer products such as bioplastics, or as platform chemicals in a number of industrial applications. The development of better ways to separate lignin from the lignocelluloses matrix during bioconversion has created the possibility of developing value-added lignin-based products as well.

The bioconversion platform uses biological agents to carry out a structured deconstruction of lignocellulose components and combines process elements of pretreatment with enzymatic hydrolysis to release carbohydrates and lignin from the wood. The first step is a pretreatment stage which must optimize the biomass feedstock for further processing. In the bioconversion platform, this step must be designed to expose cellulose and hemicellulose for subsequent enzymatic hydrolysis, increasing the surface area of the substrate for enzymatic action to take place.

Bioconversion proceeds at lower temperatures and lower reaction rates and can offer high selectivity for products. Bioethanol production is a biochemical conversion technology used to produce energy from biomass. For ethanol production, biochemical conversion researchers have focused on a process model of dilute acid hydrolysis of hemicelluloses followed by enzymatic hydrolysis of cellulose. Biodiesel production is a biochemical conversion technology used to produce energy from oilseed crops.

As in traditional pulping, lignin is either softened or removed, and individual cellulosic fibers are released creating pulp. While bioconversion pretreatment is based on existing pulping processes, however, traditional pulping parameters are defined by resulting paper properties and desired yields, while optimum bioconversion pretreatment is defined by the accessibility of the resulting pulp to enzymatic hydrolysis.

Once pretreated, the cellulose and hemicellulose components of wood can be hydrolyzed. The majority of the commercial hydrolysis programs use enzymes to facilitate fast, efficient, and economic bioconversion of the wood. Enzymatic hydrolysis of lignocellulose materials uses cellulase enzymes most commonly produced by fungi such as *Trichoderma*, *Penicillium*, and *Aspergillus*. A cocktail of cellulase enzymes is required in order to break down the cellulosic microfibril structure into its carbohydrate components in an efficient manner, unlike the bioconversion of starch, which has a simpler chemical structure. The enzymatic hydrolysis step may be completely separate from the other stages of the bioconversion process, or it may be combined with the fermentation of carbohydrate intermediates to end-products.

Separate hydrolysis and fermentation (SHF) offers the platform more flexibility, and makes it easier in theory to alter the process for different end products; however a separate process requires additional engineering and will cost more to build and operate. Simultaneous saccharification and fermentation (SSF) has been found to be highly effective in the production of specific end products, such as bioethanol.

Separation techniques are being developed to isolate the base components of cellulose, hemicellulose, and lignin in order to facilitate industrial processing of these components. Sometimes, the most effective isolation may be carried out by combining correct pretreatments with enzymatic hydrolysis.

The advantage of the bioconversion platform is that it provides a range of intermediate products, including glucose, galactose, mannose, xylose, and arabinose, which can be relatively easily processed into value-added bioproducts. The bioconversion platform also generates a quantity of lignin or lignin components; depending upon the pretreatment, lignin components may be found in the hydrolysate after enzymatic hydrolysis, or in the wash from the pretreatment stage.

Once hydrolyzed, six-carbon sugars can be fermented to ethanol using age-old yeasts and processes. Five-carbon sugars, however, are more difficult to ferment; new yeast strains are being developed that can process these sugars, but issues remain with process efficiency and the length of fermentation. Other types of fermentation, including bacterial fermentation under aerobic and anaerobic conditions, can produce a variety of other products from the sugar stream, including lactic acid.

See also: Biochemical Conversion, Biofuels – Platform, Biorefinery, Thermochemical Platform.

Biodegradation

Biodegradation (transformation of a chemical by microorganisms) is the decay or breakdown of chemicals that occurs when microorganisms use an organic substance as a source of carbon and energy. For example, sewage flows to the wastewater treatment plant where many of the organic compounds are broken down; some compounds are simply biotransformed (changed), others are completely mineralized. These biodegradation processes are essential to recycle wastes so that the elements in them can be used again. Recalcitrant materials, which are hard to break down, may enter the environment as contaminants.

Another term, biotransformation, refers to the conversion of a substance through metabolization, thereby causing an alteration to the substance by biochemical processes in an organism. Metabolism is divided into the two general categories of catabolism, which is the breaking down of more complex molecules, and anabolism, which is the building up of life molecules from simpler chemicals. The substances subjected to biotransformation may be naturally occurring or anthropogenic (made by human activities) which may consist of xenobiotic molecules that are foreign to living systems.

Biodegradation is a microbial process that occurs when all of the nutrients and physical conditions involved are suitable for growth. Temperature is an important variable; keeping a substance frozen can prevent biodegradation. Most biodegradation occurs at temperatures between 10 and 35°C (50 and 95°F), and water is essential for the biodegradation process. Bacteria and fungi, including yeasts and molds, are the microorganisms responsible for biodegradation. The biodegradation of organic matter in the aquatic and terrestrial environments is a crucial environmental process. Some organic pollutants are biocidal; for example, effective fungicides must be antimicrobial in action. Therefore, in addition to killing harmful fungi, fungicides frequently harm beneficial saprophytic fungi (fungi that decompose dead organic matter) and bacteria. Herbicides are designed for plant control, and insecticides are used to control insects.

The biodegradation process can be divided into three stages: (i) biodeterioration, (ii) biofragmentation, and (iii) assimilation. The first stage (biodeterioration) is often described as a surface-level degradation that modifies the chemical, physical, and mechanical properties of the contaminant and occurs when the material is exposed to abiotic factors in the environment and allows for further degradation by weakening the structure of the contaminant. Some abiotic factors that influence these initial changes are compression (mechanical), light, temperature, and chemicals in the environment. While biodeterioration typically occurs as the first stage of biodegradation, it can in some cases occur in parallel (simultaneously) to biofragmentation which is the conversion of the spilled chemical to lower molecular weight fragments that are more amenable to removal from the environment (or ecosystem). Assimilation occurs when the fragment (or fragments) are assimilated into the environment (or ecosystem) without any deleterious effect to the system.

The resulting products from biofragmentation can be assimilated into microbial cells; this is the assimilation stage. Some of the products from fragmentation are easily transported within the cell by membrane carriers. However, other products of the biofragmentation stage still have to undergo biotransformation reactions to yield products that can then be transported inside the cell. Once inside the cell, the products enter catabolic pathways that either lead to the production of adenosine triphosphate (ATP) or elements of the structure of the cell.

The biodegradation process is, in general, an important process for the removal of chemical compounds (especially organic chemicals) from the environment. The versatility and activity of microbial enzymes as catalysts mean that biodegradation is much more significant than purely chemical reactions such as hydrolyses and redox reactions. Enzymatically catalyzed transformation also occurs in higher organisms, but this process is quantitatively less important than the contribution from microorganisms. Some of the most important microorganism-mediated chemical reactions in aquatic and soil environments are those involving nitrogen compounds and the cycle of such compounds throughout the Earth system. Among the biochemical transformations in the nitrogen cycle are (i) nitrogen fixation, whereby molecular nitrogen is fixed as organic nitrogen, (ii) nitrification, the process of oxidizing ammonia to nitrate, (iii) nitrate reduction in which nitrogen in nitrate ions is reduced to nitrogen in a lower oxidation state, and (iv) denitrification, the reduction of nitrate and nitrite to ammonia.

Physical-chemical and biological treatment processes are employed as for wastewater treatment. In addition, chemicals are introduced for precipitation of nutrients, followed by coagulation and filtration for removing solids remaining after biological treatment. In some cases, granular activated carbon or membrane filtration or a combination of membrane-assisted solvent extraction is used for additional purification of the groundwater streams and waste streams. This higher level of treatment is advisable because of the damage that any visual traces of chemical waste can do to the appearance of the waters. In addition, the treatment may combat the potential eutrophic effect that the nutrients phosphorus and nitrogen can have on a water system.

For the most part, anthropogenic compounds resist biodegradation much more strongly than do naturally occurring compounds. This is generally due to the absence of enzymes that can cause an initial attack on the compound. A number of physical and chemical characteristics of a compound are involved in its amenability to biodegradation. Such characteristics include hydrophobicity, solubility, volatility, and affinity for lipids. Some organic structural groups impart particular resistance to biodegradation. These structural groups include branched carbon chains, ether linkages, meta-substituted benzene rings, chlorine, amines, methoxy groups, sulfonates, and nitro groups.

Usually the products of biodegradation are molecular forms that tend to occur in nature and that are in greater thermodynamic equilibrium with their surroundings than the starting materials. Detoxification refers to the biological conversion of a toxic chemical to a less toxic chemical species.

The biodegradability of a compound is influenced by its physical characteristics, such as solubility in water and vapor pressure, and by its chemical properties, including molecular mass, molecular structure, and presence of various kinds of functional groups, some of which provide a "biochemical handle" for the initiation of biodegradation. With the appropriate organisms and under the right conditions, even substances such as phenol that are considered to be biocidal to most microorganisms can undergo biodegradation.

See also: Biodegradation In Situ, Biodegradation Processes, Biodegradation – Slurry Phase, Biodegradation – Solid Phase.

Biodegradation – In Situ

In situ techniques do not require excavation of the contaminated soils, so it may be less expensive, create less dust, and cause less release of contaminants than ex situ techniques. Also, it is possible to treat a large volume of soil at once. In situ techniques, however, may be slower than ex situ techniques, may be difficult to manage, and are most effective at sites with permeable soil (i.e., sandy or uncompacted soil).

The goal of aerobic in situ biodegradation is to supply oxygen and nutrients to the microorganisms in the soil. Aerobic in situ techniques can vary in the way they supply oxygen to the organisms that degrade the contaminants. Two such methods are (i) bioventing and (ii) injection of hydrogen peroxide. Oxygen can be provided by pumping air into the soil above the water table (bioventing) or by delivering the oxygen in liquid form as hydrogen peroxide. In situ biodegradation may not work well in clays or in highly layered subsurface environments because oxygen cannot be evenly distributed throughout the treatment area. In situ remediation often requires years to reach cleanup goals, depending mainly on how biodegradable specific contaminants are. Less time may be required with easily degraded contaminants.

Bioventing systems deliver air from the atmosphere into the soil above the water table through injection wells placed in the ground where the contamination exists. The number, location, and depth of the wells depend on many geological factors and engineering considerations. An air blower may be used to push or pull air into the soil through the injection wells. Air flows through the soil, and the oxygen in it is used by the microorganisms. Nutrients may be pumped into the soil through the injection wells. Nitrogen and phosphorous may be added to increase the growth rate of the microorganisms.

Injection of hydrogen peroxide is a process that delivers oxygen to stimulate the activity of naturally occurring microorganisms by circulating hydrogen peroxide through contaminated soils to speed up the biodegradation of organic contaminants. Since it involves putting a chemical (hydrogen peroxide) into the ground (which may eventually seep into the groundwater), this process is used only at sites where the groundwater is already contaminated. A system of pipes or a sprinkler system is typically used to deliver hydrogen peroxide to shallow contaminated soils. Injection wells are used for deeper contaminated soils.

The in situ biodegradation of groundwater speeds up the natural biodegradation processes that take place in the water-soaked underground region that lies below the water table. For sites at which both the soil and groundwater are contaminated, this single technology is effective at treating both.

Generally, an in situ groundwater biodegradation system consists of an extraction well to remove groundwater from the ground, an above-ground water treatment system where nutrients and an oxygen source may be added to the contaminated groundwater, and injection wells to return the “conditioned” groundwater to the subsurface where the microorganisms degrade the contaminants. A limitation of this technology is that differences in underground soil layers and differences in the density of each of the layers may cause reinjected conditioned groundwater to follow certain preferred flow paths and, consequently, the conditioned water may not reach some areas of contamination.

Another frequently used method of in situ groundwater treatment is *air sparging* (also known as in situ air stripping and in situ volatilization), which involves pumping air into the groundwater to help flush out contaminants and is often used in conjunction with a technology called soil vapor extraction.

The air sparging method is used for the treatment of saturated soils and groundwater contaminated with volatile organic compounds (VOCs). Typically, the process involves the use of multiple air injection points and multiple soil vapor extraction points that can be installed in contaminated soils to extract vapor phase contaminants above the water table. Contamination must be at least 3 ft deep beneath the ground surface in order for the system to be effective. A blower is attached to wells, usually through a manifold, below the water table, creating pressure. The pressurized air forms small bubbles that travel through the contamination in and above water column. The bubbles of air volatilize contaminants and carry them to the unsaturated soils above. Vacuum points are installed in the unsaturated soils above the saturated zone and facilitate the extraction of the vapors through a soil vapor extraction system. In order for the vacuum to avoid pulling the air from the surface, the ground has to be covered with a tarp or other method of sealing out surface air to prevent vapors from breaking through to the surface above. Surface air intrusion into the system reduces efficiency and can reduce the accuracy of system metrics.

While the air sparging system typically treats the off-gases (referred to as contaminated vapors and extracted air), the process can also be employed to treat arsenic-contaminated groundwater treated by air sparging and what the treatment does is to remove arsenic at a certain percentage using a solution of iron and arsenic.

One of the advantages of in situ biodegradation is that it can be effectively applied to treat wastes in place. The process usually entails introduction of nutrients, microorganism, and air to the soil/waste through a series of injection wells or infiltration trenches. The term bioventing has also been applied to this technology, although the term could just as easily be applied to composting or to soil heaping.

If the soil does not have sufficient moisture content, water may also have to be added. In situ biodegradation is often applied in conjunction with groundwater pump and treat systems and soil flushing activities.

There is also the concept of gene manipulation as a means degrading polynuclear aromatic hydrocarbon derivatives. The concept offers promise for many sites (such as town gas sites where wastes containing polynuclear aromatic hydrocarbon derivatives are evident). However, the degradation products from such interactions may require cleanup. But it is quite possible that the degradation products are easier to clean than the original polynuclear aromatic hydrocarbon derivatives. There is also the concept of using biodegradation on such wastes where the waste has been reduced to residual saturation by flushing technologies. A final flushing to remove the biodegraded material will be necessary.

See also: Biodegradation, Biodegradation Processes, Biodegradation – Slurry Phase, Biodegradation – Solid Phase.

Biodegradation Processes

Biodegradation (transformation of a chemical by microorganisms) is the decay or breakdown of chemicals that occurs when microorganisms use an organic substance as a source of carbon and energy. For example, sewage flows to the wastewater treatment plant where many of the organic compounds are broken down; some compounds are simply biotransformed (changed), others are completely mineralized. These biodegradation processes are essential to recycle wastes so that the elements in them can be used again. Recalcitrant materials, which are hard to break down, may enter the environment as contaminants.

Biodegradation is a microbial process that occurs when all of the nutrients and physical conditions involved are suitable for growth. Temperature is an important variable; keeping a substance frozen can prevent biodegradation. Most biodegradation occurs at temperatures between 10 and 35°C (50 and 95°F), and water is essential for the biodegradation process. Bacteria and fungi, including yeasts and molds, are the microorganisms responsible for biodegradation. The biodegradation of organic matter in the aquatic and terrestrial environments is a crucial environmental process. Some organic pollutants are biocidal; for example, effective fungicides must be antimicrobial in action. Therefore, in addition to killing harmful fungi, fungicides frequently harm beneficial saprophytic fungi (fungi that decompose dead organic matter) and bacteria. Herbicides are designed for plant control, and insecticides are used to control insects.

The biodegradation process can be divided into three stages: (i) biodeterioration, (ii) biofragmentation, and (iii) assimilation. The first stage (biodeterioration) is often described as a surface-level degradation that modifies the chemical, physical, and mechanical properties of the contaminant and occurs when the material is exposed to abiotic factors in the environment and allows for further degradation by weakening the structure of the contaminant. Some abiotic factors that influence these initial changes are compression (mechanical), light, temperature and chemicals in the environment. While biodeterioration typically occurs as the first stage of biodegradation, it can in some cases occur in parallel (simultaneously) to biofragmentation which is the conversion of the spilled chemical to lower molecular weight fragment that are more amenable to removal from the environment (or ecosystem). Assimilation occurs when the fragment (or fragments) are assimilated into the environment (or ecosystem) without any deleterious effect to the system.

On the other hand, the resulting products from biofragmentation can be assimilated into microbial cells this is the assimilation stage. Some of the products from fragmentation are easily transported within the cell by membrane carriers. However, other products of the biofragmentation stage still have to undergo biotransformation reactions

to yield products that can then be transported inside the cell. Once inside the cell, the products enter catabolic pathways that either lead to the production of adenosine triphosphate (ATP) or elements of the structure of the cell.

By way of explanation, the catabolic pathways are those metabolic pathways that break down molecules into smaller units that are either oxidized to release energy or used in other reactions. Catabolism breaks down larger molecules into smaller units and is, in fact, the molecular breaking-down aspect of metabolism, whereas anabolic pathways are the building-up aspect.

The biodegradation of the chemicals that occur in crude oil and crude oil products is essential to the elimination of the harmful effects of these spills. This oil is degraded by both marine bacteria and filamentous fungi. The physical form of crude oil makes a large difference in its potential for degradation. Degradation in water occurs at the water-oil interface. Therefore, thick layers of crude oil prevent contact with bacterial enzymes and oxygen. Apparently, bacteria synthesize an emulsifier that keeps the oil dispersed in the water as a fine colloid and is therefore accessible to the bacterial cells.

The biodegradation process is, in general, an important process for the removal of chemical compounds (especially organic chemicals) from the environment. The versatility and activity of microbial enzymes as catalysts mean that biodegradation is much more significant than purely chemical reactions such as hydrolyses and redox reactions. Enzymatically catalyzed transformation also occurs in higher organisms, but this process is quantitatively less important than the contribution from microorganisms. Some of the most important microorganism-mediated chemical reactions in aquatic and soil environments are those involving nitrogen compounds and the cycle of such compounds throughout the Earth system. Among the biochemical transformations in the nitrogen cycle are (i) nitrogen fixation, whereby molecular nitrogen is fixed as organic nitrogen, (ii) nitrification, the process of oxidizing ammonia to nitrate, (iii) nitrate reduction in which nitrogen in nitrate ions is reduced to nitrogen in a lower oxidation state, and (iv) denitrification, the reduction of nitrate and nitrite to ammonia.

Biodegradation of phosphorus compounds is important in the environment for two reasons. The first of these is that it provides a source of algal nutrient orthophosphate from the hydrolysis of polyphosphates. Secondly, biodegradation deactivates highly toxic organophosphate compounds, such as the organophosphate insecticides. The organophosphorus compounds of greatest environmental concern tend to be sulfur-containing phosphorothionate and phosphorodithioate ester insecticides. These are used because they exhibit higher ratios of insect: mammal toxicity than do their non-sulfur analogs. The biodegradation of these compounds is an important environmental chemical process. Fortunately, unlike the organic halogen insecticides that they largely displaced, the organophosphates readily undergo biodegradation and do not accumulate.

Sulfur compounds are common in water. Sulfate ions (SO_4^{2-}) are found in varying concentration in practically all natural waters. Organic sulfur compounds, both those of natural origin and pollutant species, are common in natural aquatic systems, and the degradation of these compounds is an important microbial process. Sometimes, the degradation products, such as the odorous and toxic hydrogen sulfide, cause serious problems with water quality.

One consequence of bacterial action on metal compounds is the occurrence of drainage of acidic aqueous solutions from mines (Hall, 2006). Acid mine drainage is a common and damaging problem in the waters flowing from coal mines, and draining from the spoil piles (mine tippage, gob piles) left over from coal processing and washing is highly acidic and has the ability to sterilize the surrounding land and water systems with the ensuing serious (often fatal) effects on the flora and fauna.

Acidic mine water results from the presence of sulfuric acid produced by the oxidation of pyrite (FeS_2). Microorganisms are involved in the overall process. The prevention and cure of acid mine water is a major challenge facing the environmental chemist. Selenium is also subject to bacterial oxidation and reduction. These transitions are important because selenium is a crucial element in nutrition, particularly of livestock. Microorganisms are involved with the selenium cycle, and microbial reduction of oxidized forms of selenium has been known for some time. A soil dwelling strain of *Bacillus megaterium* has been found to be capable of oxidizing elemental selenium to selenite (SeO_3).

See also: Biodegradation, Biodegradation In Situ, Biodegradation Processes, Biodegradation – Slurry Phase, Biodegradation – Solid Phase.

Biodegradation – Slurry Phase

Slurry phase biodegradation (also known as bioreactor remediation) is a relatively more rapid process compared to the other treatment processes. The process is a controlled treatment process that involves the excavation of the contaminated soil, mixing it with water, and placing it in a bioreactor.

In the process, contaminated soil is combined with water and other additives in a large tank (the bioreactor) and mixed to keep the microorganisms, which are already present in the soil, in contact with the contaminants in the soil. Nutrients and oxygen are added, and conditions in the bioreactor are controlled to create the optimum environment for the microorganisms to degrade the contaminants. When the treatment is complete, the water is removed from the solids, which are sent for disposal or treated further if they still contain pollutants.

Slurry reactors or aqueous reactors are used for ex situ treatment of contaminated soil and water pumped up from a contaminated plume. Biodegradation in reactors involves the processing of contaminated solid material such as soil, sediment, sludge, or water through an engineered containment system.

A slurry bioreactor is a containment vessel and apparatus used to create a three- phase system, such as solid, liquid, and gas, mixing condition to increase the biodegradation rate of soil-bound pollutants and water-soluble pollutants as a water slurry of the contaminated soil and biomass capable of degrading target contaminants.

In general, the rate and extent of biodegradation are greater in a bioreactor system than in situ or in solid-phase systems because the contained environment is more manageable and hence more controllable and predictable. However, the contaminated soil may require pretreatment or, alternatively, the contaminant can be stripped from the soil via soil washing or physical extraction before being placed in a bioreactor.

See also: Biodegradation, Biodegradation In Situ, Biodegradation Processes, Biodegradation – Solid Phase.

Biodegradation – Solid Phase

Solid-phase biodegradation, often referred to as land farming, treats wastes using conventional soil management practices to enhance the microbial degradation of the wastes. Land farming is a relatively simple technique in which contaminated soil is excavated and spread over a prepared bed and periodically tilled until pollutants are degraded. The goal is to stimulate indigenous biodegradative microorganisms and facilitate their aerobic degradation of contaminants. In general, the practice is limited to the treatment of superficial 4 to 8 in. of soil. Since land farming has the potential to reduce monitoring and maintenance costs, as well as cleanup liabilities, it has received much attention as a disposal alternative. Nutrients and minerals are also added to promote the growth of the indigenous species.

Typically, the process requires excavation of contaminated soil or pumping of groundwater to facilitate microbial degradation. Ex situ biodegradation techniques involve the excavation or removal of contaminated soil from the ground. Depending on the state of the contaminant to be removed, ex situ biodegradation is classified as (i) a solid-phase system, which includes land treatment and soil piles or (ii) a slurry-phase system, which includes solid-liquid suspensions in bioreactors. A particular advantage of the ex-situ biodegradation process is that the process requires less time than the in situ process. Another advantage is the certainty of the control treatment due to the ability to uniformly screen, homogenize, and mix the soil. Ex-situ treatment technology is further divided into solid-phase biodegradation and slurry-phase biodegradation.

Solid-phase biodegradation is an ex-situ technology in which the contaminated soil is excavated and placed into piles. Bacterial growth is stimulated through a network of pipes that are distributed throughout the piles. By pulling air through the pipes, the necessary ventilation is provided for microbial respiration. Moisture is introduced by spraying the soil with water. Solid-phase systems require a large amount of space, and cleanups require more time to complete than with slurry-phase processes.

Biopiles are a hybrid of land farming and composting. Biopiles provide a favorable environment for indigenous aerobic and anaerobic microorganisms. Soil biopiles (also called biocells or bio-cells) are a biodegradation technique used for the remediation of excavated soil contaminated with crude oil and/or crude oil products. This technology involves the accumulation of contaminated soil into piles and the stimulation of microbial activity either aerobically or by the addition of nutrients, minerals or moisture. A typical height of biopiles is between 3 and 10 ft. Biopiles are

in a way similar to land farms due to the fact that this technology also uses oxygen as a way to stimulate bacterial growth. However, while tilling or plowing aerates land farms, biopiles are aerated by forcing air to move by injection through perforated piping placed throughout the pile. The soil is usually mixed with a bulking agent (such as straw) to improve aeration and therefore enhance the growth of the microbial population.

Nutrients and microorganisms are normally added to the wastes which are routinely tilled during the treatment process. This tilling improves aeration and the contact of the organisms with the wastes. While treatment may occur throughout the upper 3 to 5 ft of the soil, most occurs within the top foot, called the zone of incorporation.

Composting of chemical wastes is the biodegradation of solid or solidified materials in a medium other than soil. Bulking material, such as plant residue, paper, municipal refuse, or sawdust, may be added to retain water and enable air to penetrate to the waste material. Successful composting of chemical waste depends upon a number of factors, such as the selection of the appropriate microorganism or inoculum. Once a successful composting operation is underway, a good inoculum is maintained by recirculating spent compost to each new batch.

Other parameters that must be controlled include oxygen supply, moisture content (which should be maintained at a minimum of approximately 40% w/w), pH (usually around neutral), and temperature. The composting process generates heat, so, if the mass of the compost pile is sufficiently high, it can be self-heating under most conditions. Some wastes are deficient in nutrients, such as nitrogen, which must be supplied from commercial sources or from other wastes.

Soil heaping is piling wastes in heaps of several feet high on an asphalt or concrete pad. Nutrients, microorganisms, and air are provided through perforated piping placed throughout the pile. The pile is covered to contain volatile organic compounds, to stabilize the environment of the microorganisms, and to control soil erosion. The volatile organic compounds can be further controlled by applying a vacuum to the pile and treating the exhaust.

In this process, the wastes are normally mixed with a structurally firm bulking material such as chopped hay and wood chips. As with the other biodegradation technologies, nutrients, air, and microorganism must be added. The three major types of composting are open windrow, static windrow, and reactor systems. The differences among the three relate to how aeration is accomplished. In the open window system, the compost piles are open to the air, whereas in the static windrow system, the air is mechanically forced into the compost piles. When reactors are used, the compost is mechanically mixed to ensure aeration.

See also: Biodegradation, Biodegradation In Situ, Biodegradation Processes, Biodegradation – Slurry Phase.

BioDeNOx Process

In addition, the BioDeNOx process is a biological process removes nitrogen oxides from flue gases. An iron chelate selectively absorbs the nitrogen oxides which are reduced to nitrogen with ethanol in the presence of microorganisms. Then, a wet gas scrubber is used to contact the circulation liquid with flue gas feed and absorb the nitrogen oxides (NOx).

In the sump underneath the scrubber, the absorbed nitrogen oxides are biologically reduced to nitrogen and ethanol is also consumed and, thus, the iron chelate solution is regenerated. The presence of oxygen and acid compounds in the flue gas, such as hydrogen chloride and hydrogen fluoride, oxidizes a part of iron chelate to the ferric (Fe^{3+}) state. Therefore, a purge and makeup of iron chelate is necessary to eliminate this oxidized ferric material. To minimize iron chelate consumption, a nano-filtration can be installed and bleed from the unit is passed through the filter and the chelate is recovered.

See also: THIOPAQ DeSOx Process.

BioDesulfurization

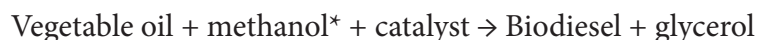
The biocatalyst desulfurization of a fuel is one of a number of possible modes of applying biologically-based processing to the needs of the renewable fuel industry. In addition, mycobacterium goodii has been found to desulfurize benzothiophene to produce α -hydroxystyrene.

Biodesulfurization is a technology to remove sulfur from the feedstock. However, several factors may limit the application of this technology. Many ancillary processes novel to crude oil refining would be needed, including a biocatalyst fermenter to regenerate the bacteria. The process is also sensitive to environmental conditions such as sterilization, temperature, and residence time of the biocatalyst. Finally, the process requires the existing hydrotreater to continue in operation to provide a lower sulfur feedstock to the unit and is more costly than conventional hydrotreating. Nevertheless, the limiting factors should not stop the investigations of the concept and work should be continued with success in mind.

See also: Refining.

Biodiesel

The term biodiesel refers to any diesel fuel substitute derived from renewable biomass. More specifically, biodiesel refers to a family of products made from vegetable oils or animal fats and alcohol, such as methanol or ethanol, called alkyl esters of fatty acids. For these to be considered as viable transportation fuels, they must meet stringent quality standards. In most contexts, unless otherwise stated, biodiesel refers to the alkyl esters produced by transesterification of vegetable oils or animal fats.



*Ethanol (ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$) could also be used.

Biodiesel is an alternative to crude oil-based fuels. Biodiesel is made from a variety of natural oils, especially rapeseed oil (a close cousin of canola oil) and soybean oil. Rapeseed oil tends to dominate the growing biodiesel industry in Europe, whereas in the United States, biodiesel is made from soybean oil because more soybean oil is produced here than all other sources of fats and oil combined. Palm and Jatropha oil are favored in Asian countries, but there are many other feedstock candidates, including recycled cooking oils, animal fats, and other oilseed crops.

Biodiesel is a renewable fuel that can be manufactured from algae, vegetable oils, animal fats, or recycled restaurant greases; it can be produced locally in most countries. It is safe, biodegradable, and reduces air pollutants, such as particulates, carbon monoxide, and hydrocarbon derivatives. Blends of 20% biodiesel with 80% crude oil diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems.

Biodiesel is made by chemically reacting vegetable oil or animal fat (or combinations of oils and fats) with alcohol (usually nearly pure methanol or ethanol) and a catalyst (sodium hydroxide). The chemical reaction converts constituents of the vegetable oil into an ester (biodiesel fuel) and glycerol. Since the biodiesel is less dense than the glycerol, it floats on top of the glycerol and may be pumped off, or the glycerol can be drained off the bottom. The fuel can then be filtered and used in heating or lighting applications. It is possible to use the product in diesel engines without further processing, but caution is advised because of the potential for engine damage and it is recommended that impurities (unreacted alcohol and sodium hydroxide) are removed by a washing.

Biodiesel is currently produced entirely from vegetable oil, waste cooking oil, animal fats, and algae. It is named biodiesel because it is derived from biological product and has similar physical properties as petro diesel. The biodiesel feedstock (oil and fats) primarily consists of triglycerides and have some amount of free fatty acids depending on their origin. The high viscosity and poor combustion properties of vegetable oils (compared to petro diesel) do not allow them to use directly as diesel substitute in engines. The direct use of vegetable oils can give rise to significant carbon deposit, lubricating oil contamination, excessive engine wear, and thus reduced engine durability. The processes such as transesterification, pyrolysis, catalytic cracking, and non-catalytic cracking have evolved to transform the vegetable oils or fats into biodiesel (fatty acid methyl ester) or biofuel.

Biodiesel is composed of long-chain fatty acids with an alcohol attached, often derived from vegetable oils. It is produced through the reaction of a vegetable oil with methyl alcohol or ethyl alcohol in the presence of a catalyst. Animal fats are another potential source. Commonly used catalysts are potassium hydroxide (KOH) or sodium hydroxide (NaOH). The chemical process is called transesterification which produces biodiesel and glycerin. Chemically, biodiesel is called a methyl ester if the alcohol used is methanol. If ethanol is used, it is called an ethyl

ester. They are similar, and currently, methyl ester is cheaper due to the lower cost for methanol. Biodiesel can be used in the pure form, or blended in any amount with diesel fuel for use in compression ignition engines.

Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield glycerin and mono-alkyl esters. If methanol is used as the alcohol for transesterification, the reaction is referred to as methanolysis and methyl esters are produced, whereas ethyl esters are produced when ethanol is used for transesterification (ethanolysis). However, it is important to point out that glycerin is considered a valuable co-product that can be used in pharmaceuticals, cosmetics, and many other applications, depending on its grade and purity. The process can be represented simply as:

Vegetable oil $\rightarrow$ transesterification/methanol $\rightarrow$ glycerol/methanol + crude biodiesel

Vegetable oil $\rightarrow$ transesterification/ethanol $\rightarrow$ glycerol/ethanol + crude biodiesel

Glycerol/methanol $\rightarrow$ refining $\rightarrow$ glycerol + methanol

Glycerol/ethanol $\rightarrow$ refining $\rightarrow$ glycerol + ethanol

Crude biodiesel $\rightarrow$ biodiesel

The process involves treatment of raw vegetable oils at low temperatures of 30 to 40°C (86 to 104°F) with methanol or ethanol in the presence of a catalyst such as sodium or potassium hydroxide (transesterification). Glycerol is produced and immediately settles out because of its low solubility in the ester product, carrying most of the dissolved catalyst with it. The upper layer containing the desired product is washed thoroughly to remove any residual catalyst and other emulsion-forming contaminants, yielding a clear, dark yellow material that can be directly used as a diesel substitute after dehydration. Phase separation can only be attained in ethanolysis under complete absence of water, whereas this process is often easier when methanol is used for transesterification.

Biodiesel may be made from virtually any oil-containing or oil-producing vegetation, including the seeds from rape, soybean, sunflower, peanut, cotton, castor and palm, or even animal fats. Other tropical oilseeds are also amenable to biodiesel production, such as *Ricinus communis* (mamona), *Jatropha curcas* (Jatropha), and *Cyperus esculentus* (tigernut). It may also be made from waste vegetable oils and fats from fish and chip or fried chicken establishments. The manufacturing process is totally benign, having no detrimental effect on the environment.

Biodiesel has a strong ecological appeal and many reasons have been claimed to support its utilization as a diesel substitute. In general, these include: (i) biodiesel is biodegradable and harmless, (ii) biodiesel can be produced from renewable materials such as vegetable oils and ethanol derived from biomass, (iii) methyl esters usually contain little sulfur (approximately 0.001% w/w) while this undesired component is literally absent in biodiesel produced by ethanolysis, (iv) biodiesel is a diesel substitute, biodiesel decreases soot emission considerably (up to 50%), (v) biodiesel emits approximately the same amount of carbon dioxide that has been absorbed during cultivation of the oilseed, (vi) biodiesel does not contain any of the carcinogenic polyaromatic components found in diesel oil, (vii) biodiesel has been recognized as a suitable outlet for the vegetable oil industry, serving as an important tool for market regulation, (viii) biodiesel can be used in blends or as a neat fuel, (ix) biodiesel is not considered as a hazardous good because it has a flash point above 110°C (230°F), (x) biodiesel has a superior lubrication capability and increases engine life, and (xi) biodiesel can be produced with a rather straight forward technology, particularly in the case of methyl esters (methanolysis).

The use of biodiesel in a conventional diesel engine also results in substantial reduction of unburned hydrocarbon derivatives, carbon monoxide, and particulate matter. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle and testing methods. The higher oxygen content of biodiesel enables a more complete combustion of the solid carbon fraction to carbon dioxide, while soluble hydrocarbon derivatives are unaffected or even increased.

Producers and users of biodiesel use the "B" factor system to state the amount of biodiesel in a fuel mix, similar to the "E" system used for fuel containing ethanol. For example, fuel containing 20% biodiesel is labeled B20, whereas pure biodiesel is referred to as B100.

See also: Bioalcohols, Biofuels – First Generation, Biofuels – Second Generation, Biofuels – Third Generation, Biogas, Vegetable Oil.

Biodiesel Feedstocks

A major focus has been and continues to be on biofuels produced from crops, such as corn, sugar cane, and soybeans, for use as renewable energy sources. Though it may seem beneficial to use renewable plant materials for biofuel, the use of crop residues and other biomass for biofuels raises many concerns related to major environmental problems, including food shortages and serious destruction of vital soil resources. Examples of feedstock for the production of biodiesel are (i) waste vegetable oil, (ii) animal fat including tallow, lard, yellow grease, chicken fat, and the by-products of the production of fatty acids from fish oil, and soybeans which are also used as a source of biodiesel (Table B-4).

Table B-4 Composition of various oils and fats used for biodiesel production.

Oil or Fat	14:0*	16:0	18:0	18:1	18:2	18:3
Corn oil	1-2	8-12	2-5	19-49	34-52	Trace
Cottonseed oil	0-2	20-25	1-2	23-35	40-50	Trace
Linseed oil		4-7	2-4	25-40	35-40	25-60
Olive oil		9-10	2-3	73-84	10-12	Trace
Peanut oil		8-9	2-3	50-60	20-30	
Safflower oil – Hi linoleic acid		5.9	1.5	8.8	83.8	
Safflower oil – Hi oleic acid		4.8	1.4	74.1	19.7	
Rapeseed oil – Hi oleic acid		4.3	1.3	59.9	21.1	13.2
Rapeseed oil – Hi erucic acid		3.0	0.8	13.1	14.1	9.7
Soybean oil		6-10	2-5	20-30	50-60	5-11
Tallow	3-6	24-32	20-25	37-43	2-3	
Yellow grease	2	23	13	44.3	7	0.7

*Indicates the number of carbon atoms in the alkyl chain and the position of the double bond.

However, for a given production line, the comparison of the feedstocks includes several issues which are (i) chemical composition of the biomass, (ii) cultivation practices, (iii) availability of land and land use practices, (iv) use of resources, (v) energy balance, (vi) emission of greenhouse gases, acidifying gases, and ozone depletion gases, (vii) absorption of minerals to water and soil, (viii) injection of pesticides, (ix) soil erosion, (x) contribution to biodiversity and landscape value losses, (xi) farm-gate price of the biomass, (xii) logistic costs such as transport and storage of the feedstock), (xiii) direct economic value of the feedstocks taking into account the co-products, (xiv) creation or maintenance of employment, and (xv) water requirements and water availability. In addition, different types of feedstocks have different types of fatty acids. The fatty acids are different in relation to the chain length, degree of unsaturation, or presence of other chemical functions, such as fatty acids.

Tropical countries have the highest potential to produce bio-fuel crops: higher energy yields, better greenhouse gas balance if properly produced, lower costs, and in some countries, large reserves of uncultivated cropland. Sugar cane and palm are the highest yielding tropical biofuel crops and consequently provide the greatest carbon offsets. Industrialized countries with biofuels targets (such as the United States and the EU countries) are unlikely to have the agricultural land base needed to meet their growing demand for current production of bio-fuels, which are largely produced from food and feed crops (e.g., maize, palm, rapeseed, soybean).

Of importance are the combustion and flow properties of biodiesel which are determined primarily by the fatty acid content of the vegetable oil which affect the fuel properties of the biodiesel. Biodiesel has lower volumetric heating values (approximately 12%) than crude oil-derived diesel fuel, but biodiesel has a high cetane number (between 46 and 70) and high flash point.

In comparison to crude oil-derived diesel, the higher cetane number of biodiesel results in (i) shorter ignition delay, (ii) longer combustion duration, (iii) low particulate emissions, and (iv) minimum carbon deposits on injector nozzles.

See also: Biochemical Platform, Biodiesel, Biofuels.

Waste cooking oil is a valuable asset for conversion to liquid fuels, and the quantity of biodiesel which could be produced from waste cooking oil can be quantified in a manner similar to that of biodiesel produced direct from agriculture. The only difference is that rather than calculating crop yields, it is necessary to quantify the amount of waste oil available.

Biodiesel is a light to dark yellow liquid that is immiscible with water and has a high boiling point, low vapor pressure, a flash point of approximately 150°C (300°F), and a density on the order of 0.88 g/cm³. Biodiesel has a viscosity similar to petrodiesel (the current term to differentiate the different forms of diesel) and can be used as an additive in formulations of diesel to increase the lubricity of pure ultra-low sulfur diesel (ULSD) fuel.

Almost any variety of oil or grease (from new food-grade vegetable oil to used cooking oil or trap grease to wastewater treatment-plant grease) can be converted into biodiesel. However, the amounts of reactants (oil, methanol, and sodium hydroxide) vary to some degree, depending on what oil is used. The amount of methanol and sodium hydroxide must be sufficient to react with the vegetable oil, but excessive amounts of these reactants should not be used. Just as an engine requires excess air to be sure that all the fuel burns, it takes excess methanol to be sure all of the oil reacts.

The chemistry of biodiesel production is known as transesterification insofar as the process involves reaction of glycoside-containing plant oil with a short chain alcohol such as methanol or ethanol. The feedstocks are typically animal, and plant fats and oils are typically made of triglycerides which are esters of free fatty acids with the trihydric alcohol, glycerol. In the transesterification reaction, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. Usually, the reaction proceeds at a low rate; heat, as well as an acid or base, is used to help the reaction proceed more quickly.

Almost all biodiesel from waste oil is produced using the base-catalyzed technique as it is the most economical process, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). The major steps required to synthesize biodiesel are purification, neutralization, and transesterification.

Purification: the waste vegetable oil is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. The crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration, but the viscosity of the oil may not allow the drying agent to mix thoroughly.

Neutralization of free fatty acids: A sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity of base required to neutralize the acid is then calculated.

Transesterification: While adding the base, a slight excess is factored in to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide) is added slowly to the alcohol, and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess is added to drive the reaction to completion. The solution of sodium hydroxide in the alcohol is then added to a warm solution of the waste oil, and the mixture is heated (typically 50°C, 122°F) for several hours (4 to 8 typically) to allow the transesterification to proceed. A condenser may be used to prevent the evaporative losses of the alcohol. Care must be taken not to create a closed system which can explode.

Workup: Once the reaction is complete, the glycerol should sink. When ethanol is used, it is reported that an emulsion often forms. This emulsion can be broken by standing, centrifugation, or the addition of a low boiling (easily removed) non-polar solvent, decanting, and distilling. The top layer, a mixture of biodiesel and alcohol, is decanted. The excess alcohol can be distilled off, or it can be extracted with water. If the latter is used, the biodiesel should be dried by distillation or with a drying agent.

See also: Biodiesel, Biodiesel Feedstocks, Biodiesel Production, Transesterification.

Biodiesel – Production and Properties

Biodiesel is a diesel-equivalent fuel derived from biological sources (such as vegetable oil) which can be used in unmodified diesel-engine vehicles. It is thus distinguished from the straight vegetable oil or waste vegetable oil used as fuels in some diesel vehicles.

Biodiesel fuel is a fuel made from the oil of certain oilseed crops such as soybean, canola, palm kernel, coconut, sunflower, safflower, corn, and a hundreds of other oil-producing crops. The oil is extracted by the use of a press and then mixed in specific proportions with other agents, which causes a chemical reaction (Figure B-1). The results of this reaction are two products, biodiesel and soap. After a final filtration, the biodiesel is ready for use. After curing, the glycerin soap which is produced as a by-product can be used as is, or can have scented oils added before use.

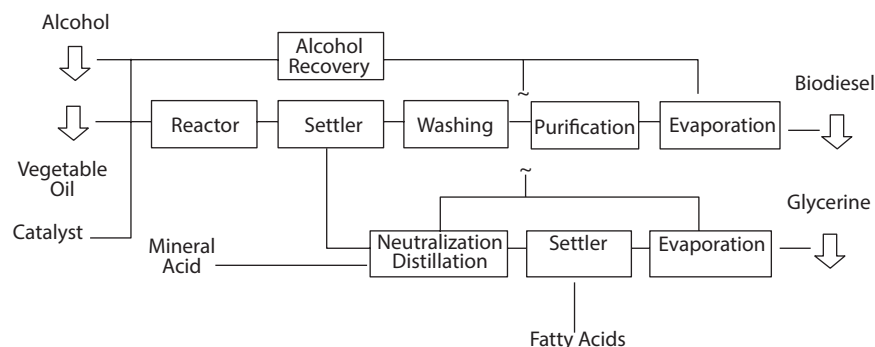


Figure B-1 Biodiesel Production Path.

Biodiesel is made through a chemical process (transesterification) whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products: (i) methyl esters and (ii) glycerin (a valuable by-product usually sold to be used in soaps and other products).

The primary products of transesterification are methyl esters (biodiesel) and glycerol. 100 lbs of soybean oil are reacted with 10 lbs of methanol and 1 lbs of catalyst yielding 100 lbs of biodiesel and 10 lbs of glycerol. Glycerol is decanted and removed first as it is heavier and sinks. Methanol is recycled in the process by washing both the glycerol and biodiesel with water to remove unreacted methanol and return it to the process. Glycerol, a valuable by-product, is approximately 88% pure and can be further processed to pharmaceutical grade glycerol.

Biodiesel is a liquid which varies in color between golden and dark brown depending on the feedstock from which it is produced. In general, biodiesel compares well to crude oil-based diesel (Table B-5). Pure biodiesel fuel (100% esters of fatty acids) is called B100. When blended with diesel fuel, the designation indicates the amount of B100 in the blend, e.g., B20 is 20% B100 and 80% diesel, and B5 used in Europe is contains 5% B100 in diesel.

Table B-5 Comparison of properties of biodiesel from various sources.

Property	Source: waste cooking oil	Source: animal tallow	Commercial diesel fuel
Density (kg/l at 15°C)	0.890 -0.897	0.856 - 0.877	0.075-0.840
Flash point (°C)	196	30 to 35	67 to 85
Pour point (°C)	11	-6 to 0	-19 to -13
Cetane number	54	58.8 - 61	40-46
Ash content (% w/w)	0.004	0.022 – 0.025	0.008-0.010
Sulfur content (% w/w)	0.06	0.18	0.35-0.55
Carbon residue (% w/w)	0.33	-	0.35-0.40
Water content (% w/w)	0.04	-	0.02-0.05

The properties of biodiesel compare very favorably with the properties of crude oil -derived diesel. For example: (i) biodiesel is a safe, non-toxic, biodegradable, and renewable fuel that produces lower regulated vehicle emissions, (ii) biodiesel is oxygenated and has a higher flashpoint making it safer to handle and store. Biodiesel also has a higher cetane number providing a smoother running engine and extending engine life, and (iii) biodiesel can also be used in locomotives, as heating oil, in generators, and as a bio-remediator in oil spills.

Biodiesel (fatty acid methyl esters; FAME) is a notable alternative to the widely used crude oil-derived diesel fuel since it can be generated by domestic natural sources such as soybeans, rapeseeds, coconuts, and even recycled cooking oil, and thus reduces dependence on diminishing crude oil fuel from foreign sources. In addition, because biodiesel is largely made from vegetable oils, it reduces lifecycle greenhouse gas emissions by as much as 78%.

Vegetable oils and animal fats belong to an extensive family of chemicals called lipids. Lipids are bio-products from the metabolism of living creatures. As a result, they can be found widely distributed in nature. Their bio-functions are diverse, but they are most known for their energy storage capacity. Most lipids can easily dissolve in common organic solvents, meaning that they are hydrophobic. If a lipid is a solid at 25°C (77°F), it is classified as a fat; otherwise, it is oil. Typically, fats are produced by animals and oils by plants, but both are mainly made of triglyceride molecules, which are tri-esters of glycerol (a triol) and free fatty acids (long alkyl chain carboxylic acids). Other glyceride species, such as di-glycerides and mono-glycerides, are obtained from triglycerides by the substitution of one and two fatty acid moieties, respectively, with hydroxyl groups.

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning every day because of the increase in the crude oil price and the environmental advantages.

Biodiesel is biodegradable and non-toxic, and typically produces approximately 60% v/v less net carbon dioxide emissions than crude oil-based diesel, as it is itself produced from atmospheric carbon dioxide via photosynthesis in plants.

It is practically immiscible with water, and has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of approximately 150°C (300°F), making it rather non-flammable. Biodiesel has a density of approximately 0.88 g/cm³, less than that of water. Biodiesel uncontaminated with starting material can be regarded as non-toxic, but it is recommended that no one drink any!

Biodiesel has a viscosity similar to diesel produced from crude oil (petrodiesel). It can be used as an additive in formulations of diesel to increase the lubricity of pure ULSD fuel, which is advantageous because it has virtually no sulfur content.

Much of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix. For example, fuel containing 20% biodiesel is labeled B20. Pure biodiesel is referred to as B100. Blends of 20% biodiesel with 80% crude oil diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems. Biodiesel has approximately 5 to 8% less energy density, but better lubricity and more complete combustion can make the energy output of a diesel engine only 2% less per volume when compared to petrodiesel.

The higher lubricity index of biodiesel compared to petrodiesel is an advantage and can contribute to longer fuel injector life. However, biodiesel is a better solvent than crude oil-derived diesel, and has been known to break down deposits of residue in the fuel lines of vehicles that have previously been run on petrodiesel. As a result, fuel filters and injectors may become clogged with particulates if a quick transition to pure biodiesel is made, as biodiesel cleans the engine in the process.

The temperature at which pure (B100) biodiesel starts to gel varies significantly and depends upon the mix of esters and therefore the feedstock oil used to produce the biodiesel. For example, biodiesel produced from varieties of canola seed starts to gel at approximately -10 °C. Biodiesel produced from tallow tends to gel at around 16°C (61°F). Winter operation is possible with biodiesel blended with other fuel oils including #2 low-sulfur diesel and #1 diesel/kerosene, but the exact blend depends on the operating environment.

Biodiesel may contain small but problematic quantities of water. Although it is hydrophobic (non-miscible with water molecules), there are indications that biodiesel is said to be, at the same time, hygroscopic to the point of attracting water molecules from atmospheric moisture. In addition, there may be water that is residual to processing or resulting from storage tank condensation. The presence of water is a problem because (i) water reduces the heat of combustion of the bulk fuel which means more smoke, harder starting, and less power, (ii) water causes corrosion of vital fuel system components: fuel pumps, injector pumps, and fuel lines, (iii) water freezes to form ice crystals at

0°C (32 °F), and the crystals provide sites for nucleation and accelerate the gelling of the residual fuel, and (iv) water accelerates the growth of microbe colonies, which can plug up a fuel system and, in fact, biodiesel users who have heated fuel tanks therefore face a year-round microbe problem.

The extra lubrication provided by biodiesel fuel helps improve the longevity of the engine, as well as boosting engine performance, also helping eliminate engine knocks and noise. In addition, biodiesel fuel can be stored in any type of tank and has a much higher flash point (approximately 300°C, 570°F) compared to petrodiesel (approximately 150°C, 300°F).

See also: Biodiesel, Biodiesel – Feedstocks, Biodiesel – Production, Biodiesel – Technical Standards.

Biodiesel – Technical Standards

The common international standard for biodiesel is EN 14214, while ASTM D6751 is the most common standard referenced in the United States and Canada (Table B-6). In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard, and in the UK, the requirements for biodiesel is fixed in the BS EN 14214 standard, although these last two standards are essentially the same as EN 14214 and are just prefixed with the respective national standards institution codes.

Table B-6 Specifications for diesel and biodiesel (ASTM).

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC* (C10–C21)	FAME** (C12–C22)
Specific gravity (g/mL)	0.85	0.88
Flash point (°C)	60–80	100 - 170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 16
Water, % v/v	0.05	0.05
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, wt%	0	11
Sulfur, wt%	0.05	0.05
Cetane number	40–55	48 - 60

*HC: hydrocarbon derivatives

**FAME: fatty acid methyl esters

There are standards for three different varieties of biodiesel, which are made of different oils: (i) rapeseed methyl ester, DIN E51606, (ii) vegetable methyl ester, purely vegetable products, DIN E51606, and (iii) fat methyl ester, vegetable and animal products, according to DIN V51606. The standards ensure that the following important factors in the fuel production process are satisfied; there needs to be (i) complete reaction, (ii) removal of glycerin, (iii) removal of catalyst, (iv) removal of alcohol, (v) absence of free fatty acids, and (vi) low sulfur content.

Basic industrial tests to determine whether the products conform to the standards typically include gas chromatography, a test that verifies only the more important of the variables above. Fuel meeting the quality standards is very non-toxic, with a toxicity rating (LD50) of greater than 50 mL/kg.

Biodiesel has promising lubricating properties and cetane ratings compared to low sulfur diesel fuels. Fuels with higher lubricity may increase the usable life of high-pressure fuel injection equipment that relies on the fuel for its

lubrication. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called *unit injectors*), and fuel injectors.

Generally, the heat content (calorific value) of biodiesel is lower than that of the regular crude oil-derived diesel, and variations in biodiesel energy density are more dependent on the feedstock used than the production process. Biodiesel can provide better lubricity and more complete combustion, thus increasing the engine energy output and partially compensating for the higher energy density of petrodiesel. The color of biodiesel ranges from golden to dark brown, depending on the production method. It is slightly miscible with water, has a high boiling point, and, consequently, a low vapor pressure. The flash point of biodiesel exceeds 130°C (266°F), which is significantly higher than that of crude oil-derived diesel which may be as low as 52°C (126°F). Biodiesel has a density of on the order of 0.88 g/cm³, higher than petrodiesel (which is approximately 0.85 g/cm³). Typically, biodiesel does not contain sulfur, and it is often used as an additive to ULSD fuel to aid with lubrication, as the sulfur compounds in petrodiesel provide much of the lubricity.

ASTM International (ASTM), formally known as the American Society for testing materials, is an international organization which develops and publishes information on the technical standards of various products, materials, systems, and services. It is one of the largest and most highly regarded standards development organizations in the world. The available literature on the performance of biofuels when compared with traditional fossil fuels normally uses ASTM and ISO (International Standards Organization) specifications and parameters. The specifications provide details on requirements for fuel characteristics as well as the relevant standard test methods to use for each.

Because of the focus on alternate fuel standards (particularly the standards for biodiesel) over the past two decades, the development of biodiesel standards started in the 1990s in order to support the increasing use of alkyl esters-based biodiesel and its blends as automotive fuels. The first ASTM standard (ASTM D6751) was adopted in 2002 while in Europe; EN 14214 biodiesel standard (based on former DIN 51606) was finalized in October 2003. The US and EU standards have international significance; they are usually the starting point for biodiesel specifications developed in other countries. However, in the United States, the standard (ASTM D6751) establishes specifications for a *biodiesel blend stock* for middle distillate fuels and, while the specification was written for B100, it is not intended for neat biodiesel used as automotive fuel. Rather, it is for the biodiesel component that is to be blended to produce biodiesel/diesel fuel blends. Since 2012, the ASTM D6751 standard has defined two grades of biodiesel (i) grade 2-B, which is identical to biodiesel defined by earlier versions of the standard, and (ii) grade 1-B, which has more strict controls on monoglycerides and cold soak filterability. In addition, the ASTM Standard Specification for Diesel Oil (ASTM D975) was modified in 2008 to allow up to 5% biodiesel to be blended into the fuel while a standard for biodiesel blends (ASTM D7467) is a specification for biodiesel blends from B6 to B20.

Most countries of the world use a system known as the “B” factor to state the amount of biodiesel in any fuel mix, in contrast to the “BA” or “E” system used for bioalcohol. Pure biodiesel is referred to as B100, while fuel containing 20% biodiesel is labeled “B20.” The common international standard for biodiesel is EN 14214, while ASTM 6751 is most referenced in the U.S. In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard.

One of the most important fuel properties of biodiesel and conventional diesel fuel derived from crude oil is viscosity, which is also an important property of lubricants. Ranges of acceptable kinematic viscosity are specified in various biodiesel and crude oil standards. Reducing viscosity is one of the main reasons why vegetable oils or fats are transesterified to biodiesel because the high viscosity of neat vegetable oils or fats ultimately leads to operational problems such as engine deposits.

The viscosity of biodiesel is slightly greater than that of petrodiesel but approximately an order of magnitude less than that of the parent starting material (vegetable oil or fat). Biodiesel and its blends with petrodiesel display temperature-dependent viscosity similar to that of neat petrodiesel. Influencing factors are chain length, position, number, and nature of double bonds as well as the nature of the oxygenated moieties.

Generally, biodiesel has a higher cloud point (temperature at which a fuel becomes hazy or cloudy and starts to gel) than petrodiesel. This makes its use impractical in cooler climates and limits its potential market. Other important chemical and physical properties described in ASTM standards for biodiesel are acid number (TAN – total acid number, indicates the presence of free fatty acids and carboxylic acids present), corrosion (describes the potential for copper corrosion, measured using ASTM method D130), low temperature performance [describes pour points (PP), and cloud points (CP) using ASTM D5949 and ASTM D5773 methods], and oxidation stability (normally evaluated using Differential Scanning Calorimetry and Oxidation Stability Index). In addition, according to the EMA (Engine

Manufacturers Association), a blend of crude oil diesel fuel meeting ASTM D975 and 100% (neat) biodiesel fuel meeting either ASTM 6751 or EN 14214, where the biodiesel content of the blended fuel is no more than 20% biodiesel by volume (B20), shall meet the requirements identified in at the point of delivery of the fuel to the end user.

In terms of the effects of biodiesel on fuel filters, use of biodiesel blends which do not meet up to the designated specifications, have shown to drastically reduce filter life. Blends greater than B20 may have enough of a solvent to break down the varnish deposits on the walls of existing fuel storage tanks or fuel systems. The breakdown of these varnish deposits will contaminate the fuel with particulate, which can cause fuel filters to plug rapidly.

Another disadvantage of biodiesel is that it tends to reduce fuel economy. Energy efficiency is the percentage of the thermal energy of the fuel that is delivered as engine output, and biodiesel has shown no significant effect on the energy efficiency of any test engine. Volumetric efficiency, a measure that is more familiar to most vehicle users, is usually expressed as miles traveled per gallon of fuel (or kilometers per liter of fuel). The energy content per gallon of biodiesel is approximately 11% lower than that of crude oil diesel. Vehicles running on B20 are therefore expected to achieve 2.2% (20 % x 11 %) fewer miles per gallon of fuel.

Areas of concern and interest are for the biofuels industry to have in place a good quality control protocol for the measurement of bioalcohols, to avoid metal corrosion from water and acid corrosion (due to weak and strong acids and inorganic chlorides in solution). Also of importance are the limits set on phosphorous content (less than 5.0 mg/L in ethanol) to prevent engine catalyst deterioration, and copper content (less than 0.1 mg/kg), along with a sulfur content less than 10 mg/kg.

Up to a 10% blend level, the performance of bioethanol-blended gasoline is similar to ordinary gasoline. At higher levels, however, some engines may begin to exhibit problems, for example, stumbling under slight acceleration. The fuel also has more aggressive properties at higher concentrations of bioethanol which increases the possibility of deterioration of some components. Gasoline must be volatile enough to move from the carburetor or injectors into the cylinders and to vaporize prior to combustion. However, gasoline cannot have such a volatility that allows it to vaporize and boil in the injectors, carburetor, fuel lines, or fuel pump, which could prevent it from being metered correctly. Also, if the gasoline is too volatile, more evaporates into the air adding to environmental problems. There are a number of volatility specifications to ensure suppliers get this balancing act right. Adding bioethanol to gasoline as low-level blends increases the volatility of the blended fuel.

The Engine Fuel Specifications Regulations specify volatility measures for bioethanol-blended petrol. The limits for blends are similar to those for gasoline so as to ensure no changes in vehicles are required. Bioethanol introduces more oxygen into the fuel. In vehicles with simple fuel metering systems such as carburetors, this causes the mixture to become a little leaner. Leaning is good for fuel economy and is generally good for lowering some types of exhaust emissions. However, it may cause some engines to stumble if they are already tuned reasonably lean. If a vehicle stumbles on bioethanol-blended gasoline, re-tuning should solve the problem. A vehicle tuned correctly for use on ordinary gasoline would normally not exhibit problems when using bioethanol blends.

See also: Biodiesel – Properties.

Biodiesel – Transesterification

Transesterification (alcoholysis) is the conversion of triacylglycerol lipids by alcohols to alkyl esters without first isolating the free fatty acids (May, 2004). The purpose of transesterification of vegetable oils to their methyl esters (biodiesel) process is to lower the viscosity of the oil. The transesterification reaction is affected by alcohol type, molar ratio of glycerides to alcohol, type and amount of catalyst, reaction temperature, reaction time, and free fatty acids and water content of vegetable oils or animal fats. The transesterification reaction proceeds with or without a catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms as follows:



Generally, the reaction temperature near the boiling point of the alcohol is recommended. The reactions take place at low temperatures (approximately 65°C, 160°F) and at modest pressures (2 atm, 1 atm = 14.7 psi). Biodiesel is further purified by washing and evaporation to remove any remaining methanol. The oil (87%), alcohol (9%), and

catalyst (1%) are the inputs in the production of biodiesel (86%), the main output. Pretreatment is not required if the reaction is carried out under high pressure (9,000 kPa) and high temperature (240°C, 465°F), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60 to 80°C (140 to 175°F) at a molar ratio of 6:1. The alcohols employed in the transesterification are generally short chain alcohols such as methanol, ethanol, propanol, and butanol. It was reported that when transesterification of soybean oil using methanol, ethanol, and butanol was performed, 96–98% of ester could be obtained after 1 hour.

Biodiesel – Transesterification, Catalytic

Transesterification reactions can be catalyzed by *alkalis* or *enzymes*. The catalytic transesterification of vegetable oils with methanol is an important industrial method used in biodiesel synthesis. Also known as methanolysis, this reaction is well established using acids or alkalis, such as sulfuric acid or sodium hydroxide as catalysts. However, these catalytic systems are less active or completely inactive for long chain alcohols. Usually, industries use sodium or potassium hydroxide or sodium or potassium methoxide as catalyst since they are relatively cheap and quite active for this reaction. Enzyme-catalyzed procedures, using lipase as catalyst, do not produce side reactions, but the lipases are expensive for industrial-scale production and a three-step process was required to achieve a 95% conversion. The acid-catalyzed process (Table B-7) is useful when a high amount of free acids is present in the vegetable oil, but the reaction time is on the order of 48 to 96 hours, even at the boiling point of the alcohol, and a high molar ratio of alcohol was needed (20:1 wt/wt to the oil).

Table B-7 Schematic of the catalytic transesterification process for biodiesel production.

Feedstock	Reactor	Products
Vegetable oil	Catalyst	Biodiesel
Methanol*		Glycerol

*Ethanol may also be used.

The transesterification process is catalyzed by alkaline metal alkoxides, and hydroxides, as well as sodium or potassium carbonates. Alkali-catalyzed transesterification with short-chain alcohols, for example, generates high yields of methyl esters in short reaction times. The alkaline catalysts show high performance for obtaining vegetable oils with high quality, but a question often arises; that is, the oils contain significant amounts of free fatty acids which cannot be converted into biodiesels but to a lot of soap. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water. Triglycerides are readily transesterified in a batch operation in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60 to 70°C (140 to 160°F) with an excess of methanol. It often takes at least several hours to ensure the alkali (NaOH or KOH) catalytic transesterification reaction is complete. Moreover, removal of these catalysts is technically difficult and brings extra cost to the final product. Nevertheless, these methods are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts since they give high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%).

The transesterification process is catalyzed by sulfuric, hydrochloric, and organic sulfonic acids. In general, acid-catalyzed reactions are performed at high alcohol-to-oil molar ratios, low-to-moderate temperatures and pressures, and high acid catalyst concentrations. These catalysts give high yields in alkyl esters, but these reactions are slow, requiring typically temperature above 100°C (212°F) and more than 3 h to complete the conversion. Studies of the acid-catalyzed system have been limited in number. Despite the relatively slow reaction rate, the acid-catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a pretreatment step. These advantages favor the use of the acid-catalyzed process when using waste cooking oil as the raw material.

Enzyme-catalyzed reactions (such as lipase-catalyzed reactions) have advantages over traditional chemical-catalyzed reactions: the generation of no by-products, easy product recovery, mild reaction conditions, and catalyst

recycling. Also, enzymatic reactions are insensitive to free fatty acids and water content in waste cooking oil. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems. The enzyme reactions are highly specific and chemically clean. Because the alcohol can be inhibitory to the enzyme, a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. The reactions are slow, with a three-step sequence requiring from 4 to 40 hours, or more. The reaction conditions are modest, from 35 to 45°C (95 to 113°F). The main problem of the enzyme-catalyzed process is the high cost of the lipases used as catalyst.

Synthesis of biodiesel using enzymes such as *Candida antarctica*, *Candida rugosa*, *Pseudomonas cepacia*, *immobilized lipase (Lipozyme RMIM)*, *Pseudomonas* sp., and *Rhizomucor miehei* is well reported in the literature. In the previously mentioned work (Shah and Gupta, 2007), the best yield 98% (w/w) was obtained by using *Pseudomonas cepacia* lipase immobilized on celite at 50°C in the presence of 4–5% (w/w) water in 8 hours.

Biodiesel – Transesterification, Supercritical Methanol

The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol, and butanol has proved to be the most promising process. Recently, a catalysts-free method was developed for biodiesel production by employing supercritical methanol (Saka and Kusdiana, 2001). The supercritical treatment at 350°C, 43 MPa, and 240 s with a molar ratio of 42 in methanol is the optimum condition for transesterification of rapeseed oil to biodiesel fuel (Kusdiana and Saka, 2004a).

To achieve more moderate reaction conditions, further effort was made through the two-step preparation. In this method, oils/fats are, first, treated in subcritical water for hydrolysis reaction to produce fatty acids. After hydrolysis, the reaction mixture is separated into oil phase and water phase by decantation. The oil phase (upper portion) is mainly fatty acids, while the water phase (lower portion) contains glycerol in water. The separated oil phase is then mixed with methanol and treated at supercritical condition to produce fatty acid methyl esters (FAMEs) thorough methyl esterification. After removing unreacted methanol and water produced in reaction, fatty acid methyl esters can be obtained as biodiesel. Therefore, in this process, methyl esterification is the main reaction for the formation of fatty acid methyl esters, while in the one-step method, transesterification is the major one.

Reaction by supercritical methanol has some advantages: (i) glycerides and free fatty acids are reacted with equivalent rates, (ii) the homogeneous phase eliminates diffusive problems, (iii) the process tolerates great percentages of water in the feedstock catalytic process and requires the periodical removal of water in the feedstock or in intermediate stage to prevent catalyst deactivation, (iv) the catalyst removal step is eliminated, and (v) if high methanol-to-oil ratios are used, total conversion of the oil can be achieved in a few minutes. Some disadvantages of the one-stage supercritical method are clear: (i) the method operates at high pressure, (ii) the high temperatures bring along proportionally high heating and cooling costs, (iii) high methanol-to-oil ratio (usually set at 42) involves high costs for the evaporation of the unreacted methanol, and (iv) the process as posed to date does not explain how to reduce free glycerol to less than 0.02% as established in the ASTM D6584 or other equivalent international standards.

Biodiesel – Transesterification, Reaction Parameters

The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time, and the contents of free fatty acids and water in oils.

The free fatty acids and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. In the transesterification, free fatty acids and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst, and reduces catalyst effectiveness, all of which result in a low conversion. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water. To carry the base catalyzed reaction to completion, a free fatty acid value lower than 3% is needed.

The presence of water has a greater negative effect on transesterification than that of the free fatty acids. In the transesterification of beef tallow catalyzed by sodium hydroxide (NaOH) in presence of free fatty acids and water, the water and free fatty acid contents must be maintained at specified levels.

The effect of reaction temperature on production of propyl oleate was examined at the temperature range from 40°C to 70°C with free *P. fluorescens* lipase (Iso et al., 2001). The conversion ratio to propyl oleate was observed highest at 60°C (140°F), whereas the activity highly decreased at 70°C (158°F).

The conversion rate increases with reaction time. The transesterification of rice bran oil with methanol was studied at molar ratios of 4:1, 5:1, and 6:1. At molar ratios of 4:1 and 5:1, there was significant increase in yield when the reaction time was increased from 4 to 6 h. Among the three molar ratios studied, ratio 6:1 gave the best results.

One of the most important factors that affect the yield of ester is the molar ratio of alcohol to triglyceride. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1, higher molar ratios are used to enhance the solubility and to increase the contact between the triglyceride and alcohol molecules. In addition, investigation of the effect of molar ratio on the transesterification of sunflower oil with methanol showed that when the molar ratio varied from 6:1 to 1:1 and concluded that 98% conversion to ester was obtained at a molar ratio of 6:1. Another important variable affecting the yield of methyl ester is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields.

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, and enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially and, quite often, for the base-catalyzed transesterification, the best yields were obtained when the catalyst was used in small concentration, i.e., 0.5% wt/wt of oil. On the other hand, during the production of free and bound ethyl ester (FAEE) from castor oil, hydrochloric acid is much more effective than sodium hydroxide

Bioenergy

Bioenergy is renewable energy produced from organic matter – the conversion of the complex carbohydrates in organic matter to energy; organic matter may either be used directly as a fuel, processed into liquids and gasses, or be a residual of processing and conversion. Bioenergy (although not quite correct) is often used interchangeably with, biofuel and biomass. More typically, the term bioenergy refers to electricity and gas that is generated from biomass, which can be any form of plants and timber to agricultural and food waste – and even sewage. The term bioenergy also covers transport fuel (biofuel) produced from organic matter.

Biofuel is fuel derived from biological sources and biomass is the biological material used as a biofuel, as well as the social, economic, scientific, and technical fields associated with using biological sources for energy. In reality, bioenergy is the energy extracted from the biomass, as the biomass is the fuel and the bioenergy is the energy contained in the fuel.

The terms bioenergy and renewable energy are often (incorrectly used) interchangeably. However, bioenergy is specific and refers to energy produced from biological course (i.e., biomass). On the other hand, renewable energy is a more collective term that includes not only bioenergy but also nuclear energy, solar energy, tidal energy, and wind energy.

Bioenergy can offer renewable, low-carbon energy systems, sequestering atmospheric carbon as well as offer numerous environmental and socioeconomic benefits and therefore supporting global climate change targets and wider environmental, social, economic, and sustainable targets.

In addition, it is important to consider various sustainable aspects of bioenergy systems beyond carbon. Ensuring that bioenergy offers the required holistic emission reduction, context, specific and long-term approaches are necessary to understand synergies and the tradeoff of the bioenergy and related agricultural and forestry systems.

See also: Biofuel, Biomass, Nuclear Energy, Solar Energy, Tidal Energy, Wind Energy.

Bioenergy Crops

Bioenergy crops are low-cost and low-maintenance crops grown solely for energy production by (for example) combustion. The crops are processed into solid, liquid, or gaseous fuels, such as pellets, bioethanol, or biogas. The fuels are burned to generate electrical power or heat. The plants are generally categorized as woody or herbaceous. The former – woody plants include willow and poplar while the latter – herbaceous plants – include miscanthus and

these crops, while physically smaller than trees, store (approximately) twice the amount of carbon dioxide (in the form of carbon) below ground, compared to woody crops.

Thus, bioenergy crops include fast-growing trees such as hybrid poplar, black locust, willow, and silver maple in addition to annual crops such as corn, sweet sorghum, and perennial grasses such as switch grass. The first-generation bioenergy crops include corn, sorghum, rapeseed, and sugarcane, whereas the second-generation bioenergy crops are comprised of switchgrass, miscanthus, alfalfa, reed canary grass, Napier grass, and other plants.

Briefly, switch grass is a thin-stemmed, warm season, perennial grass that has shown high potential as a high yielding crop that can be readily grown in areas that are also suitable for crop production. In fact, there are many perennial crops (grass and tree species) that show high potential for production of cost-competitive cellulosic biomass. Switch grass can be viewed as a surrogate for many perennial energy crops when estimating biomass supply and availability.

Bioenergy crops increase soil carbon and fix atmospheric carbon. In addition, bioenergy crops (miscanthus, sorghum, and poplar) could also be used for the phytoremediation of heavy metal-contaminated soils. The bioenergy crops include specific plants that are grown and maintained at lower costs for biofuel production. Many other crops are possible, and the optimal crop will vary with growing season and other environmental factors. Most fast-growing woody and annual crops are high in hemicellulose sugars such as xylose.

See also: Bioenergy, Biofuel, Biomass.

Bioenergy System

A bioenergy system is an energy system which is comprised of a source which generates energy and modulates it in some manner such that it conveys energy. There is also a mechanism connecting the bioenergy source to a transfer medium and a transfer medium through which the bioenergy flows. There is a coupling mechanism connecting the transfer medium bioenergy sink and a terminal sink which includes a mechanism for the storage and use of the energy. The input and output coupling depend on properties of the source and the transfer medium, likewise for the sink.

To evaluate the performance of a bioenergy system, the entire chain from biomass production up to the end-use should be considered. A major criterion for comparing total bioenergy systems is the net energy yield per hectare. If this net yield is low, the amount of land needed for the net production of a certain amount of energy is high and vice versa. Since land is a scarce commodity, high net energy yields per hectare are favored. Also, the environmental impacts of a specific energy crop are a criterion for selection. Logically, another major criterion is the cost of the biomass per GJ produced (or per GJ of fossil energy replaced).

Biomass for energy conversion is usually considered as a local resource. With appropriate logistic systems, access to biomass can be improved over a large geographical area. In this study, life cycle inventory has been used as a method to investigate the environmental load of selected bioenergy transport chains. As a case study, chains starting in Sweden and ending in Holland have been investigated. Biomass originates from tree sections or forest residues, the latter upgraded to bales or pellets. The study is concentrated on production of electricity; hot cooling water is considered as a loss.

See also: Bioenergy, Bioenergy Crops, Biomass.

Bioethanol

Bioethanol is ethanol produced from biomass feedstocks, which includes ethanol produced from the fermentation of crops, such as corn, as well as cellulosic ethanol produced from woody plants or grasses. The resource base is gradually widening to cellulosic crops, and even wood. Such low-cost feedstock would result in a global increased production potential for low-cost ethanol.

Unlike crude oil, bioethanol is a form of renewable energy that can be produced from agricultural feedstocks. It can be made from various crops such as sugar cane, potato, and maize.

The long-term prospects of bioethanol, or any other biofuels such as methanol and biodiesel, depend on biomass availability. Concerns related to its production and use relate to the large amount of arable land required for crops,

as well as the energy and pollution balance of the whole cycle of ethanol production. The availability of bioethanol depends on future food demand and food patterns, other types of land use, and agricultural productivity.

See also: Alcohols, Bioethanol Production, Ethanol.

Bioethanol Production

Bioethanol can be produced from a variety of crops, although the traditional feedstocks for the production of ethanol are still starch crops like corn, wheat and cassava and from sugar crops like sugar cane and sugar beet.

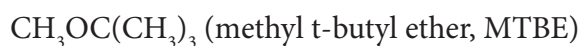
The development of lignocellulosic technology has meant that not only high energy content starch and sugar crops can be used but also woody biomass or waste residues from forestry. This process requires an additional pre-treatment process of pulping and enzymes to break down the organic compounds.

Additional steps that may be taken in a biorefinery include the drying and pelletization of bagasse (the waste component of sugar cane after juice extraction) to produce a secondary product along with ethanol, which makes the plant more economically feasible. In addition to the production of fuel pellets, one can also produce feed for animals, which could be used locally thereby reducing carbon dioxide emissions from associated transport energy spent.

See also: Alcohols, Bioethanol.

Bioethers

Ethers are a class of carbon compounds that contain an ether group (C-O-C) in which either carbon may be attached to other carbon atoms as well (such as the commonly-used diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$). The most commonly used fuel additive ethers are methyl-tertiary-butyl-ether (MTBE) and ethyl-tertiary-butyl-ether (ETBE).



Bioethers (Table B-8) are produced by the reaction of reactive iso-olefin derivatives, such as iso-butylene, with bioethanol, which is ethanol produced from bio-sources.

Table B-8 Examples of bioether derivatives used in fuels.

Ether	Use in fuels
Dimethyl ether (DME)	Alternative fuel for gasoline engines
Diethyl ether (DEE):	Used as an ignition improver for gasoline
	Possible alternative fuel for gasoline engines
Methyl tertiary-butyl ether (MTBE):	Additive for gasoline
Ethyl tert-butyl ether (ETBE):	Additive for gasoline
Tert-amyl methyl ether (TAME):	Additive for gasoline
Tert-amyl ethyl ether (TAEE):	Additive for gasoline
	Increases the solubility of ethanol in diesel

When added to gasoline, a bioether can make the gasoline burn cleanly and completely and enhance engine performance, while reducing engine wear and toxic exhaust emissions, as well as the amount of ground-level ozone.

Biofiltration

Traditional gas cleaning and air pollution control technologies for pollutant gases, such as adsorption, absorption, and combustion, were developed to treat high concentration waste gas streams associated with process emissions from stationary point sources. Although these technologies rely on established physico-chemical principles to achieve effective control of gaseous pollutants, in many cases, the control technique yields products which require further treatment before disposal or recycling of treatment materials. In the case of treatment of dilute waste gas streams, however, these traditional methods are relatively less effective, more expensive, and wasteful in terms of energy consumption and identification of alternative control measures is warranted. A suitable alternate air pollution control technology is biofiltration, which utilizes naturally occurring microorganisms supported on a stationary bed (filter) to continuously treat contaminants in a flowing waste gas stream.

Biofiltration by definition is the aerobic degradation of pollutants from (in the current context) a gas stream in the presence of a carrier media. The early development work on biofiltration technology concentrated on organic media, such as, peat, compost, and wood bark. In general terms, organic compounds are degraded to carbon dioxide and water, while inorganic compounds, such as sulfur compounds, are oxidized to form oxygenated derivatives. The formation of these acidic compounds can lead to a lowering of pH of the filtration media which in turn impacts on the performance of the system. Removal of the oxidized compound from the media is an important consideration in the design of biofiltration systems. Biofiltration, like many processes based on bio-treatment in the crude oil refining and gas processing industries, is successfully emerging as a reliable, low-cost option for a broad range of air treatment applications. It is now becoming apparent that biological treatment will play a far more significant role in achieving environmental control on air emissions.

In the biofiltration process, three types of bioreactor designs are usually considered: the biofilter, (ii) the biotrickling filter, and (iii) the bioscrubber. The main differences between these systems concern their design and mode of operation: microorganism conditioning, the nature of the fluid phase (gas or liquid), and the presence or absence of stationary solid phases. Nevertheless, gas stream desulfurization has been carried out by the biotrickling filter and the bioscrubber.

The biofilter is a pollution control technique which involves using a bioreactor that contains living material to capture and biologically degrade pollutants such as hydrogen sulfide. Common uses include processing wastewater, capturing harmful chemicals or silt from surface runoff, and the macrobiotic oxidation of contaminants in gas streams. The technology finds greatest application in treating malodorous compounds and water-soluble volatile organic compounds (VOCs). Compounds treated are typically mixed VOCs and various sulfur compounds, including hydrogen sulfide. Large airflows may be treated, although a large area (footprint) has typically been required. Engineered biofilters, designed and built since the early 1990s, have provided significant footprint reductions over the conventional flat-bed, organic media type.

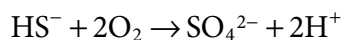
In the process, the polluted gas flow is purified with biofiltration by conducting the gas flow upward through a filter bed, which consists of biological material, e.g., compost, tree bark, or peat. The filter material is a carrier of a thin water film in which microorganisms live. The pollutants in the gas flow is held back by adsorption and/or absorption on the filter material, and then decomposed by present microorganisms. The filter material serves as a supplier of necessary nutrients. The products of the conversion are carbon dioxide, sulfate, and nitrate. The dry weight of the filter varies typically from 40 to 60 %. To reduce desiccation of the bed, the gas flow must be saturated with water. For this reason, polluted gas flow is moistened before it goes through the biofilter, which is achieved by using a pre-scrubber. The relative humidity of the gas must be 95%. In practice, it is always better to apply a moistener to protect the biofilter against dehydration.

A biotrickling filter is a packed bed bioreactor with immobilized biomass. The gas flows through a fixed bed co- or counter-currently to a mobile liquid phase. Synthetic carriers are usually used and these include plastic, ceramic, lava rocks, polyurethane foam, etc. The synthetic carrier does not provide any nutrients, so the liquid mobile phase must contain nutrients for the growth and maintenance of the biomass. Programmed or continuous discharge of

recirculation medium helps to remove the oxidation products. The hydrogen sulfide must be transferred from the gas to liquid phase, and the degradation is finally carried out in the biofilm.

According to the microbial cycling of sulfur, the biological oxidation of hydrogen sulfide to sulfate is one of the major reactions involved. There are numerous sulfur-oxidizing microorganisms, but hydrogen sulfide is exclusively oxidized by prokaryotes. In any case, the biotrickling filter is typically inoculated with aerobic active sludge, and during the process, a specific biomass population is developed.

A biotrickling filter can be operated under aerobic or anoxic conditions. The removal of hydrogen sulfide from the gas stream has been mainly studied under aerobic conditions, and the overall reaction is:

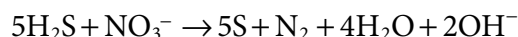


In summary, two compounds can be produced: sulfate and elemental sulfur, and the production ratio of sulfate (SO_4^{2-}) will be dependent on the oxygen-hydrogen sulfide ratio and the trickling liquid velocity. Air is used to supply oxygen and must, therefore, be supplied in excess. However, control of the air supply is an important issue for safety and operational reasons – the lower and upper explosive limits for methane in air are 5% v/v and 15% v/v, respectively.

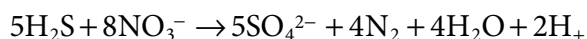
On the other hand, the gas stream can be diluted (mainly by the nitrogen content in air) and undesired residual oxygen can be found in the outlet stream. Therefore, a high oxygen supply is a drawback because the calorific power is also decreased and, moreover, a lack of oxygen increases clogging problems caused by the formation of elemental sulfur. The gas stream dilution depends on the efficiency in the mass transfer and the concentration of hydrogen sulfide. An alternative to the direct supply of air mixed with the gas stream involves the use of venture-based devices to increase the oxygen mass transfer. However, the installation of an aerated liquid recirculation system could produce hydrogen sulfide stripping of the dissolved sulfide.

The anoxic biotrickling filter is based on dissimilatory nitrate reduction. Dissimilatory nitrate reduction is carried out by certain bacteria that can use nitrate and/or nitrite as electron acceptors instead of oxygen:

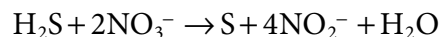
Complete denitrification vs. partial hydrogen sulfide oxidation



Complete denitrification vs. complete hydrogen sulfide oxidation



Partial denitrification vs. partial hydrogen sulfide oxidation



Partial denitrification vs. complete hydrogen sulfide oxidation



See also: Bio-oxidation, Bioscrubbing, Gas Cleaning – Biological Methods, Gas Processing, Gas Treating.

Biofuels

The term *biofuel* is a generic name for gaseous, liquid, or solid fuels that are not derived from fossil fuels or contain a proportion of non-fossil fuel. For the purposes of this text, the term alternate fuels is used to represent those fuels

that are produced from plant sources as well as from other sources such as the organic constituents' (predominantly biological in nature) municipal and industrial waste. Thus, biofuels are *bio-materials* that are produced made from renewable biological sources which are now contemplated as grown specifically for the purpose of providing useful heat upon combustion. Biofuels are produced from sources such as: corn, soybeans, flaxseed, rapeseed, sugarcane, palm oil, sugar beet raw sewage, food scraps, animal parts, and rice.

Biofuels are fuels derived from plant materials – entering the market, driven by factors such as oil price spikes and the need for increased energy security. Examples of solid biofuels include wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops, and dried manure. Biofuels are also known as non-conventional fuels or alternative fuels. Alternative fuels can be classified as any fuel that is not derived from conventional sources like natural gas, crude oil, and coal.

Other than biofuels, some more examples of alternative fuels are solar, wind and tidal power, hydrogen, air engine power, and non-conventional oil. Since mankind discovered fire, wood has been the first biofuel used for heating and cooking which has also been used to produce electricity, and liquid biofuel have been used in the automotive industry since its inception. Unlike fossil fuels, which are necessarily derived from long deceased and metamorphosed biological organisms, biofuels (otherwise known as agrofuels) are obtained from only recently deceased or from living biological organisms, or in other words, derived from biomass or bio-waste.

When raw biomass is already in a suitable form (such as firewood), it can be combusted directly in a stove or furnace to provide heat or (industrially) to raise steam. When raw biomass is in an inconvenient form (such as sawdust, wood chips, grass, urban waste wood, and agricultural residues), the typical process is to densify the biomass. This process includes grinding the raw biomass to an appropriate particulate size, which depending on the densification type can be from 0.5 to 1.5 in., which is then concentrated into a fuel product. The current types of processes are pellet, cube, or puck. The pellet process is most common in Europe and is typically a pure wood product. The other types of densification are larger in size compared to a pellet and are compatible with a broad range of input feedstocks. The resulting densified fuel is easier transport and feed into thermal generation systems such as boilers.

Bioprocessing routes have a number of compelling advantages over conventional petrochemicals production (Table B-9). However, it is only in the last decade that rapid progress in biotechnology has facilitated the commercialization of a number of plant-based chemical processes.

Table B-9 Example of sources and use of biomass for energy products.

Resources	Collection	Conversion	Products
Agricultural crops	Harvesting	Biochemical	Biodiesel
Energy crops	Collection	Thermochemical	Heat
Forestry crops		Physical processes	Electrical power
Herbaceous biomass		Chemical Processes	Other fuels
Oil-bearing plants			
Wastes			
Woody biomass			

It is widely recognized that further significant production of plant-based chemicals will only be economically viable in highly integrated and efficient production complexes producing a diverse range of chemical products. Also contrasting with fossil fuels, biofuels do not contribute to the stock of total carbon dioxide in the atmosphere, since the sources of many biofuels are plants which normally remove carbon dioxide from the atmosphere, and then give off the same amount when burned and are, therefore, considered to be carbon dioxide neutral, although some observers would doubt this balance as being the result of mathematical manipulation without taking into consideration other important and influential factors.

In any given location, the type of biofuel used will depend on, among other minor factors, the available natural resources and local energy needed for processing requirements. Some of the main reasons for the shifting of interest

from fossil fuels to biofuels are the rising prices of oil and increasing emissions of greenhouse gases, low barriers to entry of biofuels, and increasing government support. There is also a requirement for the utilization of biofuels which is the reduction or total elimination of noxious emissions in an economical manner.

Biofuels can be classified into (i) first generation biofuels, (ii) second generation biofuels, and (iii) third generation biofuels, otherwise known as advanced biofuels, and the composition varies according to the feedstock and conversion techniques used. First-generation biofuels are derived from simple materials, such as mono and disaccharides (simple sugars), amylose and amylopectin (starch), esters of glycerol and fatty acids, free fatty acids and mono and diglycerides (fats and vegetable oils for biodiesel), methanol, ethanol, propanol and butanol (bioalcohols), methyl-tertiary-butyl-ether (or MTBE) and ethyl-tertiary-butyl-ether (or ethyl-t-butyl-ether, ETBE) – also known as bioether derivatives – methane, carbon-dioxide, nitrogen, hydrogen, hydrogen sulfide, oxygen, carbon monoxide and hydrogen (synthesis gas, often referred to as syngas) and cellulose, hemicellulose derivatives and lignin (wood for solid biofuels). Second generation biofuels are typically produced by the biomass to liquid (BTL) technology and are fuels such as ethanol from lignocellulose, biohydrogen, and wood diesel. The third generation type of biofuel is a biofuel from algae otherwise known as oilgae. *Botryococcus braunii* and *Chlorella vulgaris*, as well as macroalgae (seaweed), are typically used to produce such biofuels.

In fact, the free fatty acid from non-edible oils can be mixed with crude oil-derived diesel fuel (up to 30% w/w of the non-edible oil with diesel) may be usable without having too much of an adverse effect on the properties and efficiency of the diesel fuel. However, it must be remembered that olefins in fuel (such as gasoline or diesel fuel) can often result in the form of gums that have an adverse effect on fuel flow and efficiency. This tendency can be mitigated if the fatty acids are modified to produce more suitable fuels (i.e., fuels that do not form gum products) that can act as a diesel substitute. One method involves cracking at high temperatures on certain metal oxide catalysts (decarboxylation), which yields hydrocarbon products that can be hydrogenated to the saturated hydrocarbon derivative (n-heptadecane, $C_{17}H_{36}$). Using linoleic acid as the example, the pyrolysis product is heptadecadiene which hydrogenates to heptadecane:



More generally, many food sources and plant crops are the main feedstock for biofuels, and as such, one must take into consideration the deleterious effects of biofuel production on the natural resources of any particular region. These feedstocks may enter into animal as well as human food chains, and as biofuel production has increased, there has been criticism for diverting food away from human consumption, which can lead to food shortages and increased food prices. While the demand for biofuels is directly correlated to the price of oil, other issues also arise such as deforestation, soil erosion, water usage, carbon emissions, and biofuel prices which complicate the food-vs-fuel debate with regard to energy balance and efficiency. Henceforth, while discussing the benefits of biofuels, the pitfalls must be kept apparent, before sustainable biofuel production can be realized.

In conclusion, biofuels are classed according to source and type. They are derived from forest, agricultural, or fishery products or municipal wastes, as well as from agro-industry, food industry, and food service by-products and wastes. They may be solid, such as fuelwood, charcoal and wood-pellets; liquid, such as ethanol, biodiesel and pyrolysis oils; or gaseous, such as biogas.

See also: Geothermal Energy, Hydrogen, Hydroelectric Energy, Nuclear Energy, Ocean Energy, Solar Energy, Tidal Energy, Waste, Wind Energy.

Biofuels - Classification

Put simply, a biofuel is a fuel that is produced through contemporary processes from a biological source (biomass) rather than a fuel produced by the geological processes involved in the formation of fossil fuels. In addition, the word biofuel is usually reserved for liquid or gaseous fuels, used for transportation. Biofuels can be produced from

plants (such as energy crops), or from agricultural, commercial, domestic, and/or industrial wastes (if the waste has a biological origin).

Renewable biofuel sources generally involve carbon fixation, such as those that occur in plants or in micro-algae through the process of photosynthesis. Furthermore, some observers argue that biofuel can be carbon-neutral because all biomass crops sequester carbon to a certain extent because all crops move carbon dioxide from above-ground circulation to below-ground storage in the roots and the surrounding soil. However, the simple proposal that biofuel is carbon-neutral requires that the total carbon sequestered by the root system of the energy crop must compensate for all the above-ground emissions which must include any emissions caused by direct or indirect land-use change. Many first generation biofuel projects are not carbon-neutral given these demands – in fact, some may even have higher total emissions of greenhouse gases than some fossil-based alternatives.

Generally, the classification of biofuels is related to the method of preparation which, in turn, is related to the starting material of the agent by which the biomass is converted to biofuels (Table B-10). For convenience, biofuels are generally classified as being (i) first generation biofuels, (ii) second generation biofuels, and (iii) third generation biofuels. Examples of solid biofuels include wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops, and dried manure.

Table B-10 General classification of biofuels.

1st level	2nd level	Brief definition
Woodfuels	Direct Woodfuels	Wood from forests, shrubs, and other trees
	Indirect Woodfuels	Solid biofuels produced from wood processing
	Recovered Woodfuels	Wood used directly or indirectly as fuel
	Wood-based fuels	Liquid and gaseous biofuels from woody biomass
Agrofuels	Fuel crops	Growing plants for the production of biofuels
	Agricultural by-products	By-products from crop
	Animal by-products	Primarily excreta from farm animals
	Agro-industrial by-products	Biomass as bagasse and rice husks

When raw biomass is already in a suitable form (such as firewood), it can burn directly in a stove or furnace to provide heat or raise steam. When raw biomass is in an inconvenient form (such as sawdust, wood chips, grass, urban waste wood, and agricultural residues), the typical process is to densify the biomass. This process includes grinding the raw biomass to an appropriate particulate size, which depending on the densification type can be from 1 to 3 cm, which is then concentrated into a fuel product. The current types of processes are pellet, cube, or puck. The pellet process is most common in Europe and is typically a pure wood product. The other types of densification are larger in size compared to a pellet and are compatible with a broad range of input feedstocks. The resulting densified fuel is easier to transport and feed into thermal generation systems such as boilers.

Raw biomass emits considerable amounts of pollutants such as particulate matter and polyaromatic hydrocarbon derivatives, (PAHs also known as polynuclear aromatic hydrocarbon derivative, PNAs, PAHs) during combustion. Nevertheless, biomass fuels appear to have significantly less impact on the environment than fuels based on fossil sources.

A derivative of solid biofuel is biochar, which is produced by biomass pyrolysis. Biochar made from agricultural waste can substitute for wood charcoal. As wood stock becomes scarce, this alternative fuel is gaining popularity.

In conclusion, biofuels are classed according to source and type. They are derived from forest, agricultural or fishery products, or municipal wastes, as well as from agro-industry, food industry, and food service by-products and wastes. They may be solid, such as fuelwood, charcoal, and wood-pellets; liquid, such as ethanol, biodiesel and pyrolysis oils; or gaseous, such as biogas. Table 10 gives the biofuel yields for different feedstocks and countries.

See also: Alcohols, Algae Fuel, Bioalcohol, Bioethanol, Biodiesel.

Biofuels - Feedstocks

Currently, there is a focus on biofuels made from crops, such as corn, sugar cane, and soybeans, for use as renewable energy sources. Though it may seem beneficial to use renewable plant materials for biofuel, the use of crop residues and other biomass for biofuels raises many concerns related to major environmental problems, including food shortages and serious destruction of vital soil resources. Tropical countries have the highest potential to produce biofuel crops: higher energy yields, better greenhouse gas (GHG) balance if properly produced, lower costs, and in some countries, large reserves of uncultivated cropland. Sugar cane and oil palm are the highest-yielding tropical biofuel crops and consequently provide the greatest carbon offsets. Industrialized countries with biofuels targets (such as the United States and the European Union countries) are unlikely to have the agricultural land base needed to meet their growing demand for current production of biofuels, which are largely produced from food and feed crops (e.g., maize, oil palm, rapeseed, soy).

Bioethanol feedstocks can be divided into three major groups: (i) sucrose-containing feedstocks, such as sugar cane, sugar beet, sweet sorghum, and fruits, (ii) starchy materials, such as corn, milo, wheat, rice, potatoes, cassava, sweet potatoes, and barley, and (iii) lignocellulosic biomass, such as wood, straw, and grasses). In the short term, the production of bioethanol as a vehicular fuel is almost entirely dependent on starch and sugars from existing food crops. The drawback in producing bioethanol from sugar or starch is that the feedstock tends to be expensive and demanded by other applications as well.

Sugarcane as a bio-fuel crop has much expanded in the last decade, yielding anhydrous bio-ethanol (gasoline additive) and hydrated bio-ethanol by fermentation and distillation of sugarcane juice and molasses. The yield of ethanol per hectare, is on the order of 7,000 L per hectare. Brazil is the largest single producer of sugarcane with approximately 31% of the global production and millions of hectares (1 ha = 2.47 ac) of sugarcane under cultivation. Brazilian bio-ethanol is less expensive than that produced in the United States from corn or in Europe from sugar beet, because of shorter processing times, lower labor costs, and lower transport costs and input costs.

Another type of feedstock, which can be used for bioethanol production, is starch-based materials. Starch is a high yield feedstock for bioethanol production, but its hydrolysis is required to produce bioethanol by fermentation. Starch is a biopolymer, defined as a homopolymer consisting of only one monomer, D-glucose. The starch-based bioethanol industry has been commercially viable for approximately 30 years; in that time, tremendous improvements have been made in enzyme efficiency, reducing process costs and time, and increasing bioethanol yields. This type of feedstock is the most utilized for bioethanol production in North America and Europe. Corn and wheat are mainly employed with these purposes. Corn-based bioethanol production in most of the countries assessed is limited, especially compared to the United States.

There is also interest in a large amount of studies regarding the utilization of lignocellulosic biomass as a feedstock for producing fuel ethanol is being carried out worldwide. For countries where the cultivation of energy crops is difficult, lignocellulosic materials are an attractive option for the production of biofuels. Lignocellulosic materials serve as a cheap and abundant feedstock, which is required to produce fuel ethanol from renewable resources at reasonable costs. Producing bioethanol from lignocellulosic materials may allay many of the environmental and food-versus-fuel concerns that are drawbacks of producing bioethanol from food crops like sugar or corn.

Biodiesel has been mainly produced from renewable oil crops such as soybean, rapeseed, mustard seed oil, sunflower oil, and jatropha as well as from recycled vegetable oils and animal fats. The benefits of biodiesel also depend on the type of oilseed used. Seeds of high oil content, such as sunflower (40 to 50% w/w oil), rapeseed (42 to 48% w/w oil), and soybean seeds (18 to w/w 20% oil) have gained much attention lately as renewable energy sources because of their relatively high yield per hectare.

Biodiesel from oil crops is being produced in increasing amounts as a clean-burning alternative fuel, but its production in large quantities is not sustainable. Microalgal biofuels are a viable alternative. Microalgae are photosynthetic microorganisms that convert sunlight, water, and carbon dioxide to algal biomass. Algae have the potential to dwarf all the other biodiesel feedstocks due to their efficiency in photosynthesizing solar energy into chemical energy. Many algae are exceedingly rich in oil, which can be converted to bio-diesel. In fact, the oil productivity of many microalgae often exceeds the best-producing oil crops. The oil content of some microalgae exceeds 80% of dry

weight of algae biomass. Oil levels on the order of 20 to 50% w/w are quite common, and microalgae with high oil productivities are desired for producing biodiesel.

Biofuels – First Generation

First-generation biofuels are biofuels produced from sugar, starch, vegetable oil, or animal fats using conventional technology. The oil is obtained using the conventional techniques of production. Some of the most popular types of first-generation biofuels are: biodiesel, vegetable oil, biogas, bioalcohols, and synthesis gas.

Biodiesel has a composition similar to fossil/mineral diesel except that components in biodiesel include animal fats and oils from soy, mustard, flax, and sunflower seeds. The oil or animal fat is reacted with an alcohol through a process called transesterification to create the fuel. Vegetable oil is most often used in the production of biofuels, but there are cases where straight vegetable oil is being used as a fuel.

Biogas is created when organic matter breaks down anaerobically (that means without any oxygen). It can be produced from gunk like manure, sewage, and municipal waste. Some types of biogas, such as landfill gas, contain something called volatile organic compounds that are restricted by environmental regulations. Synthesis gas (syngas) is a mix of carbon dioxide and hydrogen. It is created when biomass is combusted with a measured (limited) amount of oxygen. Syngas can be used to produce diesel and can also be converted into methane.

Bioalcohols are produced through the fermentation of starches and sugars. Ethanol is the most common bioalcohol, although there is also methanol, propanol, and butanol. Some bioalcohols can be used directly in gasoline-powered engines.

The basic feedstocks for the production of first-generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel. These feedstocks could instead enter the animal or human food chain, and as the global population has increased, their use in producing biofuels has been criticized for diverting food away from the human food chain, leading to food shortages and price rises.

The most common first-generation biofuels are bioalcohols, biodiesel, biogas, and vegetable oil.

See also: Bioalcohols, Biodiesel, Biofuels From Synthesis Gas, Biofuels – Second Generation, Biofuels – Third Generation, Biogas, Methanol, Ethanol, Vegetable Oil.

Biofuels – From Synthesis Gas

Biomass can be converted into fuels and chemicals indirectly (by gasification to syngas followed by catalytic conversion to liquid fuels) or directly to a liquid product by thermochemical means. The process yields synthesis gas (syngas) composed primarily of hydrogen and carbon monoxide, also called biosyngas.

The production of high-quality syngas from biomass, which is later used as a feedstock for biomass-to-liquids (BTL) production, requires particular attention. This is due to the fact that the production of synthesis gas from biomass is indeed the novel component in the gas-to-liquids concept – obtaining syngas from fossil raw materials (natural gas and coal) is a relatively mature technology.

Gasification is actually thermal degradation of the feedstock in the presence of an externally supplied oxidizing (oxygen-containing) agent e.g., air, steam, oxygen. Various gasification concepts have been developed over the years, mainly for the purposes of power generation. However, efficient biomass-to-liquids production imposes completely different requirements for the composition of the gas. The reason is that in power generation, the gas is used as a fuel, while in biomass-to-liquids processing, it is used as a chemical feedstock to obtain other products. This difference has implications with respect to the purity and composition of the gas.

In contrast, for biomass-to-liquids production, the amount of carbon monoxide and hydrogen is only important (the larger the amount, the better), while the calorific value is irrelevant. The presence of other hydrocarbon derivatives and inert components should be avoided or at least kept as low as possible. This can be achieved in the following ways: (i) by adjusting the amount of the various constituents of the gas stream, (ii) choice of the oxidizing agent.

The amount of components other than carbon monoxide and hydrogen (primarily hydrocarbon derivatives) can be reduced via further transformation into carbon monoxide and hydrogen. This is, however, rather energy intensive and costly (two processes – gasification and transformation). As a result, the overall energy efficiency of syngas production and of biomass-to-liquids processing is also reduced, leading to higher production costs.

The amount of various components can be minimized via a more complete decomposition of biomass, thereby preventing the formation of undesirable components at the gasification step. The minimization of the content of various hydrocarbon derivatives is achieved by increasing temperatures in the gasifier, along with shortening the residence time of feedstocks inside the reactor. Because of this short residence time, the particle size of feedstocks should be small enough (in any case – smaller than in gasification for power generation) in order that complete and efficient gasification can occur.

In gasification for power generation, typically, air is employed as oxidizing agent, as it is indeed the cheapest among all possible oxidizing agents. However, the application of air results in large amounts of nitrogen in the product gas, since nitrogen is the main constituent of air. The presence of such large quantities of nitrogen in the product gas does not hamper (very much) power generation, but it does hamper biomass-to-liquids production. Removing this nitrogen via liquefaction under cryogenic temperatures is extremely energy intensive, reduces substantially the overall biomass-to-liquids energy efficiency and increases costs. Amongst other potential options (steam, carbon dioxide, oxygen), from a technical and economic point of view oxygen appears to be the most suitable oxidizing agent for biomass-to-liquids manufacturing. It is true that the oxygen-blown gasification implies additional costs compared to the air-blown gasification, because of the oxygen production. Nevertheless, the energy and financial cost of producing oxygen seems to be far lower than the renewable energy and financial cost of cleaning up the product gas from air-blown gasification from nitrogen. This is partly due to the fact that the production of high-purity oxygen (above 95% O₂) is a mature technology.

In principle, the larger the carbon and hydrogen content in raw materials, employed in gas-to-liquids processing, is, the easier and more efficient the carbon monoxide and hydrogen. Hence, the natural gas pathway is the most convenient one since natural gas is gaseous and contains virtually carbon and hydrogen only. Solid raw materials (biomass, coal) involve more processing, because first they have to be gasified and then the product gas should be cleaned up from other components such as nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter to the extent of getting as high as possible purity of syngas.

Two basic types of biomass raw material are distinguished, viz, woody material and herbaceous material. Currently, woody material accounts for approximately 50% of total world bioenergy potential. Another 20% is straw-like feedstock, obtained as a by-product from agriculture. The dedicated cultivation of straw-like energy crops could increase the herbaceous share up to 40%.

See also: Bioalcohols, Biodiesel, Biofuels – First Generation, Biofuels From Synthesis Gas, Biofuels – Second Generation, Biofuels – Third Generation, Biogas, Gasification, Methanol, Ethanol, Vegetable Oil.

Biofuels – Liquid

Liquid biofuels, as their name suggests, are fuels derived from biomass and processed to produce a combustible liquid fuel. There are two main categories: (i) alcohol fuels, such as methanol and ethanol, and (ii) vegetable oils, which are derived from plant seeds, such as sunflower, sesame, linseed, and rapeseed.

Methanol is produced by a process of chemical conversion from any biomass with a moisture content of less than 60%. Potential feedstocks include forest and agricultural residues, wood, and various energy crops. As with ethanol, it can either be blended with gasoline to improve the octane rating of the fuel or used in its neat form. Both methanol and ethanol are often preferred fuels for racing cars.

Ethanol is the most widely used liquid biofuel and is produced by fermentation of sugars and starches or cellulosic biomass. Most commercial production of ethanol is from sugar cane or sugar beet, as starches and cellulosic biomass usually require expensive pre-treatment. Ethanol is used as a renewable energy fuel source as well as being used for manufacture of cosmetics, pharmaceuticals, and also for the production of alcoholic beverages.

Vegetable oils are used to produce biodiesel. The process of oil extraction from the biomass is carried out the same way as for extraction of edible oil from plants. There are many crops grown in rural areas of the developing world

which are suitable for oil production – sunflower, coconut, cotton seed, palm, rapeseed, soy bean, peanut, hemp, and more. Sunflower oil, for example, has an energy content approximately 85% that of diesel fuel.

There are two well-established technologies for oil extraction: (i) the screw press and (ii) solvent extraction. The simple screw press, which is a device for physically extracting the oil from the plant - this technology is well suited to small-scale production of oil as fuel or as foodstuff in rural areas. The press can be motor-driven or hand-operated. On the other hand, solvent extraction is a chemical process which requires large, sophisticated equipment. This method is more efficient - that is, it extracts a greater percentage of the oil from the plant - but is less suited to rural applications.

Biodiesel production is not complex – the vegetable oil is converted to a useable fuel by adding ethanol or methanol alcohol along with a catalyst to improve the reaction. Small amounts of potassium hydroxide or sodium hydroxide (commonly called lye or caustic soda, which is used in soap making) are used as the catalyst material. Glycerine separates out as the reaction takes place and sinks to the bottom of the container. This removes the component that gums up the engine so that a standard diesel engine can be used. The glycerine can be used as a degreasing soap or refined to make other products.

See also: Bioalcohols, Biodiesel, Biofuels, Cellulosic Biomass, Methanol, Ethanol, Vegetable Oil.

Biofuels – Platforms

The technical platform chosen for second-generation biofuel production will be determined in part by the characteristics of the biomass available for processing. The majority of terrestrial biomass available is typically derived from agricultural plants and from wood grown in forests, as well as from waste residues generated in the processing or use of these resources. Much of the biomass being used for first-generation biofuel production includes agricultural crops that are rich in sugars and starch. Because of the prevalence of these feedstocks, the majority of activity toward developing new products in the United States has focused on the bioconversion platform.

Bioconversion isolates sugars from biomass, which can then be processed into value-added products. Native sugars found in sugarcane and sugar beet can be easily derived from these plants, and refined in facilities that require the lowest level of capital input. Starch, a storage molecule which is a dominant component of cereal crops such as corn and wheat, is comprised wholly of glucose. Starch may be subjected to an additional processing in the form of an acid- or enzyme-catalyzed hydrolysis step to liberate glucose using a single family of enzymes, the amylases, which makes bioconversion relatively simple. Downstream processing of sugars includes traditional fermentation, which uses yeast to produce ethanol; other types of fermentation, including bacterial fermentation under aerobic and anaerobic conditions, can produce a variety of other products from the sugar stream.

Forest biomass or agricultural residues are almost completely comprised of lignocellulosic molecules (wood), a structural matrix that gives the tree or plant strength and form. This type of biomass is a prime feedstock for combustion, and indeed remains a major source of energy for the world. The thermochemical platform utilizes pyrolysis and gasification processes to recover heat energy as well as the gaseous components of wood, known as synthesis gas (or syngas) which can then be refined by the Fischer-Tropsch process into synthetic fuels such as hydrocarbon liquids, methanol, and ethanol.

Lignocellulose is a complex matrix combining cellulose, hemicellulose, and lignin, along with a variable level of extractives. Cellulose is comprised of glucose, a six-carbon sugar, while hemicellulose contains both five- and six-carbon sugars, including glucose, galactose, mannose, arabinose, and xylose. The presence of cellulose and hemicellulose therefore makes lignocellulose a potential candidate for bioconversion. The ability of the bioconversion platform to isolate these components was initially limited, as the wood matrix is naturally resistant to decomposition. Recent advances, however, have made this process more commercially viable. Costs remain higher than for starch-based bioconversion, but there is added potential for value-added products that can utilize the lignin component of the wood.

In order to incorporate all aspects of biofuel production, including the value of co-products and the potential of the industry to diversify their product offering, we employ the biorefinery concept. The biorefinery concept is important because it offers many potential environmental, economic, and security-related benefits to society. Biorefineries provide the option of co-producing high-value, low-volume products for niche markets together with

lower-value commodity products, such as industrial platform chemicals, fuels, or energy, which offsets the higher costs that are associated with processing lignocellulosic materials.

The two technological platforms being explored for the lignocellulose-based biorefinery are complementary. Each technological platform provides different intermediate products for further processing. It is the range of these intermediates that dictates the types of end products that are likely to be successful in a commercial sense.

See also: Bioalcohols, Bioconversion Platform, Biodiesel, Biogas, Fischer-Tropsch Process, Thermochemical Platform, Vegetable Oil.

Biofuels – Production

There is some concern related to the energy efficiency of biofuel production. Production of biofuels from raw materials requires energy (for farming, transport, and conversion to final product), and it is not clear what the overall efficiency of the process is. For some biofuels, the energy balance may even be negative.

Since vast amounts of raw material are needed for biofuel production, monocultures and intensive farming may become more popular, which may cause environmental damages and undo some of the progress made toward sustainable agriculture.

See also: Bioconversion Platform, Thermochemical Platform.

Biofuels – Properties, Variations with Source

The quality and composition of a biofuel depends on the source of the biomass/feedstock as well as the types of processing and conversion techniques utilized in its manufacture. Biomass feedstock composition ultimately decides the yield from the chemical or biochemical conversion processes, which in turn, affects the economics involved. There are many plant varieties which are used as biofuel sources - the geography, weather conditions, soil composition, and legislation of a location normally dictates what types are grown specifically for biofuel production. Ethanol, biodiesel, and butanol are the main types of commercially produced biofuels.

The soil organic matter content contributes greatly to the grain and stover, and hence carbohydrate content of maize plants. Lignin and cell-wall cross-linking also affect the ethanol production. Selection for reduced lignin and increased cellulose in stover can potentially be expected to increase mechanical strength as well as ethanol yield. Although pretreatment and enzyme hydrolysis constitute two of the more costly steps in cellulosic ethanol production, stover with reduced lignin may still need to be treated before being subjected to enzyme hydrolysis. It seems unlikely that the cost savings in pretreatment from reduced lignin can be fully realized because of an accompanying reduction in biomass. However, for ethanol production to be commercially viable, improvements must not only be made to the efficiency of ethanol production per unit dry mass, but also per unit land area.

Biomass feedstock composition ultimately decides the yield from the chemical or biochemical conversion processes, which in turn, affects the economics involved. There are many plant varieties which are used as biofuel sources - the geography, weather conditions, soil composition, and legislation of a location normally dictates what types are grown specifically for biofuel production. Ethanol, biodiesel, and butanol are the main types of commercially produced biofuels.

The soil organic matter content contributes greatly to the grain and stover, and hence carbohydrate content of maize plants. Lignin and cell-wall cross-linking also affects the ethanol production. Selection for reduced lignin content and increased cellulose content in stover can potentially be expected to increase mechanical strength as well as ethanol yield. Although pretreatment and enzyme hydrolysis constitute two of the more costly steps in cellulosic ethanol production, stover with reduced lignin may still need to be treated before being subjected to enzyme hydrolysis.

The production of biofuels from lingo-cellulosic feedstocks can be achieved through two very different processing routes which are (i) the biochemical route in which enzymes and other micro-organisms are used to convert cellulose and hemicellulose components of the feedstocks to sugars prior to their fermentation to produce ethanol and (ii) the thermochemical route in which pyrolysis and gasification technologies produce a synthesis gas (carbon

monoxide, CO, and hydrogen, H₂) from which a wide range of long chain biofuels, such as synthetic diesel or aviation fuel, can be reformed. One key difference between the biochemical and thermochemical routes is that lignin component is a residue of the enzymatic hydrolysis process and can be used for heat and power generation.

Genetics as well as environmental factors affect the chemical composition of the various parts of the plant, and it was found that husk, followed by rind and pith, has the highest sugar (glucan + xylan) content. The term glucan represents diverse glucose polymers that differ in the position of glycosidic bonds, which can be short or long, branched or unbranched, alpha or beta isomers, and soluble or insoluble. On the other hand, the term represents a group of hemicellulose derivatives.

The variation in the structure of the glucan derivatives and the xylan derivatives (Figure B-2) is due to differences in the amounts of the main chemical constituents of biomass (cellulose, hemicelluloses, and lignin, all of which have different uses) being present in different proportions in the various parts of the plant.

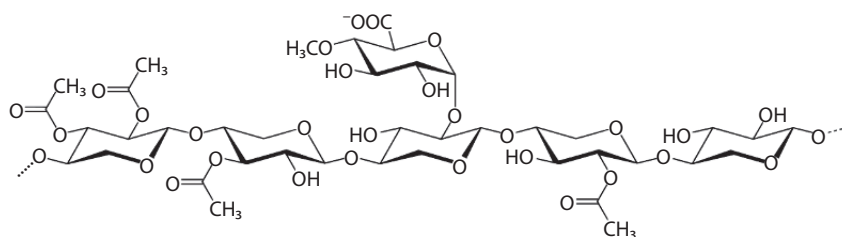


Figure B-2 Structure of xylan from hardwood.

The production of fuels from ligno-cellulosic feedstocks can be achieved through two different processing routes. These are (i) biochemical, whereby enzymes and other microorganisms are used to convert cellulose and hemicellulose components of the feedstocks to sugars prior to their fermentation to produce ethanol and (ii) the thermochemical route, where pyrolysis and gasification technologies produce a synthesis gas (carbon monoxide and hydrogen) from which a wide range of long chain biofuels, such as synthetic diesel or aviation fuel, can be reformed. In terms of the biochemical route, much remains to be done related to (i) improving feedstock characteristics, (ii) improving the efficiency of enzymes, and (iii) improving overall process integration. One key difference between the biochemical and thermochemical routes is that lignin component is a residue of the enzymatic hydrolysis process and can be used for heat and power generation.

In terms of the production of biodiesel, transesterification optimization is desired, which would depend on the chemical composition of alkyl esters of vegetable oils, animal fats, and cooking oil. Most common feedstocks possess fatty acid profiles consisting mainly of five C₁₆ and C₁₈ fatty acids, namely, palmitic (hexadecanoic), stearic (octadecanoic), oleic (9(Z)-octadecenoic), linoleic (9(Z),12(Z)-octadecadienoic), and linolenic (9(Z),12(Z),15(Z)-octadecatrienoic) acids, with the exception of a few oils such as coconut oil, which contains high amounts of saturated acids in the C₁₂ to C₁₆ range. Changing the fatty acid profile can be achieved by physical means, genetic modification of the feedstock, or use of alternative feedstocks with different fatty acid profiles, such as wood-derived fatty-acids and related compounds.

The production of biogas is essentially achieved by wastewater treatment facilities which use anaerobic digestion to reduce the organic content of sewage sludge and animal wastes. The variation in the composition of biogas will depend on the organic content of the biomass as well as the pretreatment and processing. In addition to the main components (methane and carbon dioxide), biogas can also contain a variety of contaminants and impurities, such as sulfur compounds (hydrogen sulfide, mercaptans), halogens, ammonia, and dust particles.

Concerning biodiesel production, transesterification optimization is desired, which would depend on the chemical composition of alkyl esters of vegetable oils, animal fats, and cooking oil. Most common feedstocks possess fatty acid profiles consisting mainly of five C₁₆ and C₁₈ fatty acids, namely, palmitic (hexadecanoic), stearic (octadecanoic), oleic (9(Z)-octadecenoic), linoleic (9(Z),12(Z)-octadecadienoic), and linolenic (9(Z),12(Z),15(Z)-octadecatrienoic) acids, with the exception of a few oils such as coconut oil, which contains high amounts of saturated acids in the C₁₂ to C₁₆ range or others. Changing the fatty acid profile can be achieved by physical means, genetic modification of

the feedstock, or use of alternative feedstocks with different fatty acid profiles, such as wood-derived fatty acids and related compounds.

Bio-oil can be used directly as fuel or can be fractionated to obtain purified hydrocarbon derivatives boiling in the range of gasoline and diesel fuel – analysis of waste fish oil has shown that the main composition of fatty acids is: $C_{16:0}$ (15.9% w/w), $C_{18:2}$ (20.9% w/w), $C_{18:1}$ (17.3% w/w), $C_{20:5}$ (5.1% w/w), $C_{20:1}$ (7.6% w/w), $C_{22:6}$ (4.3% w/w), and $C_{22:1}$ (10.4% w/w) – the first number in the carbon-related subscript is the chain length and the second number is the position of the double bond in the carbon chain. Other compounds were classified as paraffin derivatives (4.5% w/w), iso-paraffin derivatives (8.3% w/w), olefin derivatives (26.6% w/w), naphthene derivatives (6.1% w/w), and aromatic derivatives (16.9% w/w).

Tall oil is a dark, viscous, and odorous liquid that phase-separates from the used pulping liquor (alkaline black liquor) that remains after the pulping of wood chips, and contains sodium soaps of rosin and fatty acids. Fish oil is also a potentially good source of fatty acids for the production of bio-oil. In a particular study, waste fish oil was converted into bio-oil by a fast pyrolysis process at 525°C (975°F) in a continuous pilot plant reactor with a yield on the order of 72% yield. Many different chemical groups can be produced during the pyrolysis reaction, and the liquid product (bio-oil) obtained from triglyceride pyrolysis has a complex composition. This bio-oil can be used directly as fuel or can be fractionated to obtain purified hydrocarbon derivatives in the range of gasoline and diesel.

Green algae (aquatic and unicellular) biomass is also used in biodiesel production, and is an attractive source of triglycerides, as under good conditions, green algae can double its biomass in less than 24 hours. Factors such as carbon dioxide availability, sunlight, water, and space affect algal density, and the annual productivity and oil content of algae are far greater than seed crops.

One of the largest issues seems to be overall greenhouse gas emissions from the various biofuels when compared with crude oil fuels. To estimate the impacts of increases in renewable and alternative fuels on greenhouse gas emissions, the entire fuel lifecycle including fossil fuel extraction or feedstock growth, fuel production, distribution, and combustion should be taken into consideration to provide a comparison of the carbon dioxide emissions from different fuels.

It is generally accepted that biofuels have the potential to drastically lower carbon-dioxide emissions than fuels derived from crude oil, but in many instances, this is not the case. For example, ethanol made from corn requires a substantial amount of energy in terms of fertilization, irrigation, harvesting and fermentation processes and most of this energy comes from fossil fuels. As a result, some ethanol production scenarios emit more lifecycle carbon-dioxide emissions than gasoline. Cellulose-based ethanol, however, allows for more efficient and cost-effective fuel production, and the carbon footprint is decreased. Conversely, biodiesel blended into diesel at low levels reduces emissions of volatile organic compounds, carbon monoxide, particulate matter, and sulfur oxides during combustion. Further, over the full life cycle, biodiesel blends reduce carbon monoxide, particulate matter, and sulfur oxides compared with diesel.

The bulk density (related to energy density) of most solid biomass feedstocks is generally low, even after compression, and is approximately between 10 and 40% of the bulk density of most fossil fuels; however, liquid biofuels have comparable values. Since biomass materials are more reactive, with higher ignition stability, they are generally easier to gasify and thermochemically process into methanol and hydrogen (higher-value fuels). Coal ash may contain toxic metals and small amounts of other trace contaminants, while biomass ash may be used as a soil amendment to assist in replacing nutrients removed by harvest. Bioethanol possesses approximately 70% of the heating value of crude oil distillates, but its sulfur and ash contents are appreciably lower.

Ethanol has a lower energy density than gasoline, so for a given volume of gasoline, a larger volume of ethanol is needed to produce an equivalent amount of energy. Unfortunately, when ethanol is used to power vehicles, it leads to lower gas mileage, since energy density is correlated with gas mileage. Ethanol, which has approximately a 30% lower energy density than gasoline, contributes to a reduction in fuel mileage when it is mixed with gasoline, as now commonly practiced in the United States. Another problem with ethanol as an auto fuel is it is extremely hygroscopic. Ethanol is difficult to separate from water and readily absorbs water from its surrounding. This is a problem in the transport and storage of ethanol, as well as the purification of ethanol from water. Ethanol-containing fuels can easily absorb water, and decontamination (i.e., removal of water from fuel) is difficult. The difference between the properties of gasoline and ethanol also causes compatibility problems in engines. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the United States Clean Air Act.

The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbon derivatives, carbon monoxide, and particulate matter compared to emissions from diesel fuel. In addition, the exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel. Of the major exhaust pollutants, both unburned hydrocarbon derivatives and nitrogen oxides are ozone or smog-forming precursors. The use of biodiesel results in a substantial reduction of unburned hydrocarbon derivatives. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used.

Based on engine testing, using the most stringent emissions testing protocols required by EPA for certification of fuels or fuel additives in the US, the overall ozone-forming potential of the speciated hydrocarbon emissions from biodiesel was nearly 50% less than that measured for diesel fuel. In a review published in 2009,⁴³ the environmental indicators related to biofuel production were examined.

The postulated superior properties of agrofuels when compared with fossil fuels, as we have seen, must be weighed very carefully among the various factors of cost, environmental impact, energy density, chemical composition and availability, and life cycle of food crops. No doubt, increasing advances in technology will tip the scales in favor of biofuels.

In terms of fuel properties, one of the largest issues seems to be overall greenhouse gas emissions from the various biofuels when compared with crude oil fuels. To estimate the impacts of increases in renewable and alternative fuels on greenhouse gas emissions, it is necessary to account for the entire fuel lifecycle including fossil fuel extraction or feedstock growth, fuel production, distribution, and combustion.

The fuels are compared on an energy equivalent or Btu basis. Thus, for instance, for every Btu of gasoline which is replaced by corn ethanol, the total lifecycle greenhouse gas emissions that would have been produced from that Btu of gasoline would be reduced by 21.8%. These emissions account not only for CO₂, but also methane and nitrous oxide.

It is generally accepted that biofuels have the potential to drastically lower carbon-dioxide emissions than fuels derived from crude oil, but in many instances, this is not the case. For example, ethanol made from corn requires a substantial amount of energy in fertilization, irrigation, harvesting, and fermentation processes and most of this energy comes from fossil fuels. As a result, some ethanol production scenarios emit more lifecycle carbon-dioxide emissions than gasoline. Cellulose-based ethanol, however, allows for more efficient and cost-effective fuel production, and the carbon footprint is decreased.

However, the use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel. In addition, the exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel. Of the major exhaust pollutants, both unburned hydrocarbons and nitrogen oxides are ozone or smog-forming precursors. The use of biodiesel results in a substantial reduction of unburned hydrocarbons. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used.

The postulated superior properties of agrofuels when compared with fossil fuels, as we have seen, must be considered and compared very carefully among the various factors of cost, environmental impact, energy density, chemical composition, and availability and life cycle of food crops.

Biofuels – Second Generation

Second-generation biofuel production processes can use a variety of non-food crops. These include waste biomass, the stalks of wheat, corn, wood, and special-energy-or-biomass crops (e.g., *Miscanthus*). Second-generation biofuels use biomass-to-liquid technology, including cellulosic biofuels from non-food crops. Second-generation biofuels include biohydrogen, biomethanol, Fischer-Tropsch diesel, mixed alcohols, and wood diesel.

Second-generation biofuels (also called advanced biofuels) made from nonfood sources hold significant promise as a low-carbon, renewable transportation fuel that can complement traditional crude oil-based fuels in meeting the future energy needs of the world. Technologies that can convert cellulosic biomass, often regarded as a waste material, into transportation fuels are becoming popular. Examples of cellulosic biomass include: (i) agricultural wastes,

such as corn stalks and husks, (ii) forestry wastes, such as wood chips and tree trimmings, (iii) fast-growing trees and grasses grown as energy crops, (iv) waste paper, and (v) food processing wastes

Although using cellulosic biomass as a source of new transportation fuels has obvious advantages, these materials have different chemical structural bonds than food-based crops and are difficult to break down, especially on a large scale. These second-generation fuels may play an important role in diversifying the energy sources of the world and curbing greenhouse gas emissions.

Cellulosic ethanol production uses non-food crops or inedible waste products and does not divert food away from the animal or human food chain. Lignocellulose is the woody structural material of plants. This feedstock is abundant and diverse, and in some cases represents a significant disposal problem. The discovery of the fungus *Gliocladium roseum* points toward the production of so-called myco-diesel from cellulose. This organism was recently discovered in the rainforests of northern Patagonia and has the unique capability of converting cellulose into medium length hydrocarbon derivatives typically found in diesel fuel.

See also: Biofuels – First Generation, Biofuels – Third Generation.

Biofuels – Specifications and Performance

ASTM International (ASTM), formally known as the American Society for testing materials, is an international organization which develops and publishes information on the technical standards of various products, materials, systems, and services. It is one of the largest and most highly regarded standards development organizations in the world. The available literature on the performance of biofuels when compared with traditional fossil fuels normally uses ASTM and ISO (International Standards Organization) specifications and parameters. The specifications provide details on requirements for fuel characteristics as well as the relevant standard test methods to use for each. The common international standard for biodiesel is EN 14214, while ASTM 6751 is most referenced in the United States. In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard.

With regards to biodiesel, most of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix, in contrast to the “BA” or “E” system used for bioalcohol. Pure biodiesel is referred to as B100, while fuel containing 20% biodiesel is labeled B20.

The standards ensure that the following important factors in the fuel production process are satisfied: (i) complete reaction, (ii) removal of glycerin, (iii) removal of catalyst, (iv) removal of alcohol, and (v) ensuring the absence of free fatty acids. Basic industrial tests to determine whether the products conform to the standards typically include gas chromatography, a test that verifies only the more important of the variables above. Fuel meeting the quality standards is very non-toxic, with a toxicity rating (LD50) greater than 50 mL/kg.

One of the most important fuel properties of biodiesel and conventional diesel fuel derived from crude oil is viscosity, which is also an important property of lubricants. Ranges of acceptable kinematic viscosity are specified in various biodiesel and crude oil standards. Reducing viscosity is one of the main reasons why vegetable oils or fats are transesterified to biodiesel because the high viscosity of neat vegetable oils or fats ultimately leads to operational problems such as engine deposits. The viscosity of biodiesel is slightly greater than that of petrodiesel but approximately an order of magnitude less than that of the parent vegetable oil or fat. Biodiesel and its blends with petrodiesel display temperature-dependent viscosity similar to that of neat petrodiesel. Influencing factors are chain length, position, number and nature of double bonds, as well as the nature of the oxygenated moieties.

Classic biodiesel has a higher cloud point (temperature at which a fuel becomes hazy or cloudy and starts to gel) than petrodiesel. This makes its use impractical in cooler climates and limits its potential market. Other important chemical and physical properties described in ASTM standards for biodiesel are (i) total acid number, TAN, which indicates the presence of free fatty acids and carboxylic acids present, (ii) corrosion, which is the potential for copper corrosion, (iii) low temperature performance, which is described by the pour point and the cloud point, and (iv) oxidation stability.

In terms of the effects of biodiesel on fuel filters, use of biodiesel blends which do not meet up to the designated specifications, have shown to drastically reduce filter life. Blends greater than B20 may have enough of a solvent to break down the varnish deposits on the walls of existing fuel storage tanks or fuel systems. The breakdown of these varnish deposits will contaminate the fuel with particulate, which can cause fuel filters to plug rapidly.

Another disadvantage of biodiesel is that it tends to reduce fuel economy. Energy efficiency is the percentage of the fuel's thermal energy that is delivered as engine output, and biodiesel has shown no significant effect on the energy efficiency of any test engine. Volumetric efficiency, a measure that is more familiar to most vehicle users, is usually expressed as miles traveled per gallon of fuel (or kilometers per liter of fuel).

Approximately 11% of the weight of B100 is oxygen. The presence of oxygen in biodiesel improves combustion and therefore reduces hydrocarbon, carbon monoxide, and particulate emissions; but oxygenated fuels also tend to increase nitrogen oxide emissions. Engine tests have confirmed the expected increases and decreases of each exhaust component from engines without emission controls.

Areas of concern and interest are for the biofuels industry to have in place a good-quality control protocol for the measurement of bioalcohols, to avoid metal corrosion from water and acid corrosion (due to weak and strong acids and inorganic chlorides in solution). Also of importance are the limits set on phosphorous content (less than 5.0 mg/L in ethanol) to prevent engine catalyst deterioration, and copper content (less than 0.1 mg/kg), along with a sulfur content less than 10 mg/kg.

Up to a 10% blend level, the performance of bioethanol-blended petrol is similar to ordinary gasoline. At higher levels however, some engines may begin to exhibit problems, for example, stumbling under slight acceleration. The fuel also has more aggressive properties at higher concentrations of bioethanol which increases the possibility of deterioration of some components. Gasoline must be volatile enough to move from the carburetor or injectors into the cylinders and to vaporize prior to combustion. However, it can't be so volatile that it vaporizes and boils in the injectors, carburetor, fuel lines, or fuel pump, which could prevent it from being metered correctly. Also, if gasoline is too volatile, it evaporates into the air adding to environmental problems. There are a number of volatility specifications to ensure suppliers get this balancing act right. Adding bioethanol to gasoline as low-level blends increases the volatility of the blended fuel.

The Engine Fuel Specifications Regulations specify volatility measures for bioethanol-blended gasoline and gasoline. The limits for blends are similar to those for gasoline so as to ensure no changes in vehicles are required. Bioethanol introduces more oxygen into the fuel. In vehicles with simple fuel metering systems such as carburetors, this causes the mixture to become leaner which is advantageous for fuel economy and for lowering some types of exhaust emissions. However, it may cause some engines to stumble if they are already tuned reasonably lean. If a vehicle stumbles on bioethanol-blended gasoline, re-tuning should solve the problem. A vehicle tuned correctly for use on ordinary gasoline would normally not exhibit problems when using bioethanol blends.

The factors of availability, price, and independence of manufacturer, health benefits, engine improvements, and political implications must all be carefully weighed and assessed, before educated decisions can be made by the powers that be. It is hoped however, that despite some of the obvious setbacks of biofuel production, that it is still viewed as a step in the right direction, and emerging technologies and innovative ideas will encourage improvements in what is undoubtedly, the future of fuel.

Biofuels – Third Generation

Third-generation biofuels (also called advanced biofuels) seek to improve the feedstock, rather than improving the fuel-making process.

Designing oilier crops, for example, could greatly boost yield. Scientists have designed poplar trees with lower lignin content to make them easier to process. Researchers have already mapped the genomes of sorghum and corn, which may allow genetic agronomists to tweak the genes controlling oil production.

Algae fuel, also called oilgae or third-generation biofuel, is a biofuel from algae, which are low-input, high-yield feedstocks that can produce biofuels. Algae can produce up to 30 times more energy per acre than land crops such as soybeans. With the higher prices of fossil fuels, there is much interest in algaculture (farming algae).

One advantage of many biofuels over most other fuel types is that they are biodegradable, and so relatively harmless to the environment if spilled. Algae fuel still has its difficulties though, for instance, to produce algae fuels, it must be mixed uniformly, which, if done by agitation, could affect biomass growth. Algae, such as *Botryococcus braunii* and *Chlorella vulgaris*, are relatively easy to grow, but the algal oil is difficult to extract. Macroalgae (seaweed) also have a great potential for bioethanol and biogas production.

Recently, the term fourth-generation biofuels has arisen and is coming into popular use. Fourth-generation technology combines genetically optimized feedstocks, which are designed to capture large amounts of carbon, with genomically-synthesized microbes, which are made to efficiently make fuels. The key to the process is the capture and sequester of carbon dioxide, a process that renders fourth-generation biofuels a carbon negative source of fuel. However, the weak link is carbon capture and sequestration technology, which continues to challenge industry.

See also: Biofuels – First Generation, Biofuels – Second Generation

Biofuels – Use

Biomass has the potential to supply a considerable portion of the energy needs of the world, but the conversion of biomass to energy is carried out in an unsustainable manner that there are many negative environmental consequences. If biomass is to supply a greater proportion of the energy needs in the future, the challenge will be to produce biomass and to convert and use it without harming the natural environment. Technologies and processes exist which, if used correctly, make biomass-based fuels less harmful to the environment than fossil fuels. Applying these technologies and processes on a site-specific basis in order to minimize negative environmental impacts is a prerequisite for sustainable use of biomass energy in the future.

Biodiesel and bioethanol are widely used in automobiles and freight vehicles. For example, in Germany, most diesel fuel on sale at gas stations contains a few percent biodiesel, and many gas stations also sell 100% biodiesel. Some supermarket chains in the UK have switched to running their freight fleets on 50% biodiesel, and often include biofuels in the vehicle fuels they sell to consumers, and an increasing number of service stations are selling biodiesel blends (typically with 5% biodiesel).

In Europe, research is being undertaken into the use of biodiesel as domestic heating oil. A blend of 20% biodiesel with 80% kerosene (B20) has been tested successfully to power modern high efficiency condensing oil boilers. Boilers needed a preheat burner to prevent nozzle blockages and maintain clean combustion. Blends with a higher proportion of biodiesel were found to be less satisfactory, owing to the greater viscosity of biodiesel than conventional fuels when stored in fuel tanks outside the building at typical (non-arctic) winter temperatures.

See also: Biodiesel, Biofuels, Ethanol, Methanol.

Biogas

Biogas, which is also known as biomethane, landfill gas, swamp gas, and digester gas, is a collection of gases (largely methane and carbon dioxide) produced by the anaerobic degradation of biomass (non-fossil organic matter) by various bacteria (Table B-11).

Thus, biogas is a combustible gas derived from decomposing biological waste under anaerobic conditions. Biogas typically refers to a biofuel gas produced by anaerobic digestion or fermentation of organic matter including manure, sewage sludge, municipal solid waste, biodegradable waste, or any other biodegradable feedstock, under anaerobic conditions. Depending on where it is produced, biogas is also called swamp gas, marsh gas, landfill gas, and digester gas (Table B-9).

Table B-11 The composition of gas from various carbonaceous fuels.

Composition:	Digester gas	Landfill gas	Sewage gas	Agri-waste
Carbon Dioxide (CO ₂)	25-45%	35-50%	30-40%	25-45%
Methane (CH ₄)	45-65%	40-45%	55-65%	55-75%
Nitrogen (N ₂)	2-5%	0-20%	2-10%	0-10%

The primary component of biogas is methane gas, which comprises 50-90% by volume of biogas. Usually, biogas is 50% to 80% methane and 20% to 50% carbon dioxide, with the remainder trace gases such as hydrogen,

carbon monoxide, and nitrogen. Methane is also the primary component of natural gas, but natural gas is normally recovered with more than 70% methane, along with other hydrocarbons (such as butane and propane) and traces of carbon dioxide and other chemicals. Natural gas is processed so that it is almost entirely, 98%, methane. Biogas is produced in a variety of low-oxygen natural environments with degradable organic matter, including swamps, marshes, landfills, agricultural and other waste (sewage sludge, manure, waste lagoons), aquatic sediments, wet soils, buried organic matter, as well as via enteric fermentation in some animal digestive tracts, notably in cattle.

Biogas normally consists of 50 to 60% methane and has a variable composition and energy content (Btu/ft³) depending upon the source (Table B-12).

Table B-12 Energy content of various gases.

Coal seam gas (coalbed methane): 370-955 Btu/ft ³
Digester gas: 275-700 Btu/ft ³
Landfill gas: 275-700 Btu/ft ³
Manufactured gas (coal gas): 160-955 Btu/ft ³
Wood chip gas: 160-320 Btu/ft ³

Biogas is produced by means of a process known as anaerobic digestion – a process in which organic matter is broken down by microbiological activity in the absence of air. Biogas is generated from concentrations of sewage or manure. These are usually in the form of slurry comprised mostly of water (almost 95%). The slurry is fed into a digester, this input can be continuous (usually the case with sewage) or in batches. The digestion continues from approximately 10 days up to weeks. The temperature in the digester should be kept at 35°C (95°F), and although the digestion itself produces heat, in colder climates, heat may be necessary.

There are two common technologies for the production of biogas. The first involves the fermentation of human and/or animal waste in specially designed digesters:

Slurry → digester → biogas

The second is a more recently developed technology for capturing methane from municipal waste landfill sites. The scale of simple biogas plants can vary from a small household system to large commercial plants. The digestion of animal and human waste yields several benefits: (i) the production of methane for use as a fuel and (ii) the waste is reduced to slurry which has a high nutrient content which makes an ideal fertilizer, and in some cases, (iii) the fertilizer is the main product from the digester and the biogas is merely a by-product. During the digestion process, bacteria in the manure are killed, which is a great benefit to environmental health.

Two popular simple designs of digester have been developed: (i) the floating cover digester and (ii) fixed dome digester. The digestion process is the same in both digesters, but the gas collection method is different in each. In the floating cover digester, the water-sealed cover of the digester is capable of rising as gas is produced and acting as a storage chamber, whereas the fixed dome digester has a lower gas storage capacity and requires good sealing if gas leakage is to be prevented.

The waste fed into the digester undergoes digestion in the digestion chamber and the temperature of the process is quite critical – methane-producing bacteria operate most efficiently at temperatures between 30 and 40°C (86 to 104°F) or 50 and 60°C (122 to 140°F), and in colder climates, heat may have to be added to the chamber to encourage the bacteria to carry out their function. The product is a combination of methane and carbon dioxide, typically in the ratio of 6:4. Digestion time ranges from a week to months depending on the feedstock and the digestion temperature. The residual slurry is removed at the outlet and can be used as a fertilizer.

The composition of biogas varies depending upon the composition of the waste material in the landfill and the anaerobic digestion process. Landfill gas typically has methane concentrations around 50%. Advanced waste treatment technologies can produce biogas with 55 to 75% methane; often, air is introduced (5% by volume) for microbiological desulfurization. For example, the constituents (by volume) of biogas generally are methane (50 to 75%),

carbon dioxide (25 to 50%), nitrogen (0 to 10%), hydrogen (0 to 1%), hydrogen sulfide (0 to 3%), and oxygen (0 to 2%).

If biogas is cleaned up sufficiently, biogas has the same characteristics as natural gas. In this instance, the producer of the biogas can utilize the local gas distribution networks. The gas must be clean to reach pipeline quality. Water (H_2O), hydrogen sulfide (H_2S), and particulates are removed if present at high levels or if the gas is to be completely cleaned. Carbon dioxide is less frequently removed, but it must also be separated to achieve pipeline quality gas. If the gas is to be used without extensively cleaning, it is sometimes co-fired with natural gas to improve combustion. Biogas cleaned up to pipeline quality is called renewable natural gas and can be used in any application in which natural gas is used.

Current technology allows the gas to be recovered using sealed vessels and therefore available for heating, electrical generation, mechanical power, and so forth. Biogas can be retrieved from garbage or mechanical biological treatment waste processing systems. The solid by-product, digestate, can be used as a biofuel or a fertilizer. Like natural gas, biogas has a low volumetric energy density compared to liquid biofuels, but it can be purified to a natural gas equivalent and further compressed for use as a transportation fuel, substituting for natural gas. Methane is also suitable for use in fuel cell generators. Biogas is often made from wastes, but is also made from biomass energy feedstocks. Landfill gas cannot be distributed through utility natural gas pipelines unless it is cleaned up to less than 3% v/v carbon dioxide and several parts per million hydrogen sulfide, because these chemicals corrode the pipelines.

See also: Aerobic Digester, Anaerobic Digester, Landfill Gas.

Biogas – Upgrading

Biogas upgrading principally refers to removal of the carbon dioxide from the biogas to increase energy density and decrease needed storage volumes of finished product. Moisture, sulfur compounds, organo-silicon compounds (siloxanes), and other impurities in biogas or fuel gas are usually removed as well to meet gas quality specifications, and because they can cause problems in gas handling equipment and damage engines and emissions controls. Biomethane from upgraded biogas or landfill gas can be compressed or liquefied and used as a fuel in compressed natural gas (CNG) or liquefied natural gas (LNG) vehicles.

Processes available for separating carbon dioxide from the methane in biogas include adsorption methods such as scrubbing with water, Selexol (polyethylene glycol ether), and amines, pressure swing absorption (PSA), membrane separation, and cryogenic separation. However, each biogas project is unique it can be a challenge to determine the best gas upgrading technology for the given situation. Digester biogas can have varying levels of carbon dioxide (CO_2) and elevated hydrogen sulfide (H_2S) to address. Landfill gas and gas from covered lagoon digesters can have elevated nitrogen (N_2) and oxygen (O_2) levels, and landfills and municipal wastewater treatment plant (WWTP) digesters have siloxanes that need to be handled.

Typically, biogas is usually fully saturated with water vapor and typically has from 40 to 60% methane (CH_4) and 40 to 60% v/v carbon dioxide (CO_2). Thus, the choice of an appropriate technology or combination of technologies to upgrade the gas from these modest methane levels up to 99% v/v methane can be challenging. The main treatment goal of gas upgrading projects is to get the carbon dioxide removed from the biogas stream to an acceptable level, typically on the order of with 1 to 2% v/v carbon dioxide. Actual specifications will vary based on end use and the specific requirements provided by the gas utility.

Selecting an upgrading system that can reliably meet the methane-oxygen-carbon dioxide-hydrogen sulfide specifications is critical for a successful relationship with one's gas off-taker. At times, such as at a new project site, technologies may need to be selected without having extensive biogas characterization data. Therefore, selecting a biogas upgrading system that can handle varying gas quality and quantity and stay within specifications is essential.

The preferred design approach is to design for existing biogas streams that allow for maximum data collection for the upfront characterization of the gas. Generally, gas is pretreated to remove water and hydrogen sulfide from the biogas stream before the gas the stream is fed to the upgrading process(es). Where appropriate, users should consider drying biogas through aggressive refrigeration techniques or desiccant drying. Hydrogen sulfide can be effectively removed by several techniques, including ferric chloride injection in the digester, chemical scrubbing, carbon filtration, iron-based media filtration, or biological desulfurization. Digester biogas and landfill gas containing traces

of siloxanes requires pretreatment through media filtration. In all cases, the pretreatment system needs to be evaluated to ensure that it does not interfere with the gas upgrading system.

In terms of water content, biogas from a digester has just emerged from a warm, liquid process so it is fully saturated with water. Water vapor, or steam, is dissolved in the gas to its highest degree possible, and thus the gas is extremely damp and humid, containing approximately 6 to 12% w/w water. Warm gas holds more water vapor than cool gas. Dew point is the measure used to describe the condition where steam starts to condense into liquid. High dew point (i.e., $>21^{\circ}\text{C}$, $>70^{\circ}\text{F}$) gas is indicative of very humid gas that is acceptable to send to wet upgrading systems. Low dew point (i.e., $<-29^{\circ}\text{C}$, $<-20^{\circ}\text{F}$) gas is indicative of very dry gas that is acceptable to send to dry upgrading systems. However, each of the upgrading systems is capable of meeting gas pipeline or vehicle fuel specifications, either as standalone units or in combination with each other.

There are four main technologies used to create the so-called renewable natural gas stream from biogas, and these are (i) membrane separation, (ii) pressure swing adsorption (PSA), (iii) amine scrubbing, and (iv) water wash, also known as water scrubbing. Typically, these processes are usually deployed individually but can sometimes be installed in a series with one another, as needed for the given project requirements.

The membrane system and the pressure swing adsorption system are somewhat similar as both are dry upgrading systems that involve a physical separation of the carbon dioxide and methane based on (i) molecular size, (ii) pressure, and (iii) ionic charge, if any. Water wash and amine systems are similar in that they are both wet upgrading systems and involve separating the carbon dioxide from the methane by solubilizing the carbon dioxide in a liquid solution while allowing the methane to remain in the gas phase.

Membrane Separation

The membrane separation technique uses polymeric membranes to separate the carbon dioxide from the methane in biogas while under high pressure. As a result of the process, there is (i) permeate gas, which is the gas that has traveled through the porous membrane and (ii) retentate gas, which is gas that is retained and collected at the end of the membrane fiber; this gas travelled down the path of the membrane lumen hole but did not travel through the porous membrane. In recent years, membrane manufacturers have improved manufacturing quality, improved membrane selectivity, and overall system methane recovery. These factors all lead to better overall system performance, improved economics, and increased opportunity for success.

For landfill gas or covered lagoon applications, separating nitrogen from methane is challenging with membranes; therefore, further gas polishing is required when there is a significant amount of nitrogen in the raw biogas. In addition, biogas oxygen levels can cause performance issues as membranes are not selective for separating oxygen. For example, sources of oxygen can be a less-than-airtight landfill or leaky covered lagoon, as well as leaking fittings on the suction side of compressing equipment.

A typical pretreatment option uses an activated carbon filter to remove hydrogen sulfide to a level <100 parts per million (ppm) and removal of volatile organic compounds (VOCs). Drying can be achieved by refrigerating the gas to 4 to 15°C (40 to 60°F) and capturing the resulting condensate. The volatile organic compounds should be free of any volatile organic compounds which can irreversibly foul or compromise some membrane types.

Pressure Swing Adsorption

The pressure swing adsorption (PSA) system is a batch process utilizing several vessels running in parallel under pressure. The heart of the process is an adsorptive medium, similar to activated carbon, which separates the constituents of the gas stream based on the molecular weight and size of the constituents. Predrying the gas ahead of the adsorbers to approximately 5°C (41°F) is required to keep the humidity out of the vessels to maximize their performance as dry adsorbers.

Carbon dioxide is preferentially adsorbed onto the media because it is a smaller molecule than methane and can permeate into the tiny pores in the carbon bed more easily and deeply. The methane goes through adsorber process columns relatively untouched, while the carbon dioxide does not. The adsorption process is reversible; thus, the carbon dioxide is eliminated during the regeneration cycle.

When a vessel has been saturated with contaminant gas, it is regenerated by reducing the pressure. At lower pressure, compounds are removed and desorbed from the media in a separate gas stream called "tail gas." The common cycle time to saturation is 2 to 4 minutes. The tail gas is a low-quality gas stream that contains the previously adsorbed

compound (such as carbon dioxide, hydrogen sulfide, and methane). Each vessel alternates its mode of operation from service, depressurization, regeneration, and finally repressurization before it returns to service mode.

Amine Scrubbing

The amine scrubbing system uses a two-step approach to upgrading biogas. The first step is adsorption followed by a second step of stripping or desorption. The amine portion of the scrubbing solvent molecule chemically reacts to the carbon dioxide in the biogas to retain it in solution. A common chemical deployed as the scrubbing solvent is monoethanolamine (MDEA). The methane fraction of the biogas passes through the packed tower reactor untouched by the scrubbing chemical. High methane purities can be achieved in the recovered natural gas (>99.9% v/v).

In the second step, the scrubbing solution is heated to boiling to reverse the chemical reaction. The carbon dioxide in the fully packed stripper tower is disassociated from the scrubbing solution and discharged. High carbon dioxide purity in the off-gas can be achieved to accommodate potential for reuse of the carbon dioxide. The regenerated amine scrubbing solution is then cooled and reused back in the scrubbing tower in a closed loop system. Systems run at a relatively low operating pressure of approximately 0.5 to 3 psi. This low-pressure design affords equipment and operational savings as compared to systems that run at high pressure. Raw biogas with a high content (>300 ppm) of hydrogen sulfide is recommended to be pretreated by any one of several desulfurization techniques.

The recovered methane is dehumidified through a desiccant dryer and then pressurized to supply the natural gas grid. Pressurization power consumption is lower than for systems that use gas compression ahead of the scrubbing system since just the recovered methane is compressed versus the total raw biogas flow in other systems.

Water Wash

The water wash system is a two-stage process much like amine systems. The first step is a high-pressure reactor column that works in a countercurrent fashion. Chilled water flows downward and biogas flows upward under high pressure (150 psig). Soluble gases such as carbon dioxide dissolve in the water. The second tower serves as a depressurization tower where pressure is released from the solution and carbon dioxide comes out of solution. Makeup water is added when needed. Blow-down water is purged from the system to maintain the desired pH and water quality.

This system is run as a wet process; thus, no predrying of the biogas is formally required but is recommended. Any hydrogen sulfide in the biogas stream is adsorbed in the process after which the hydrogen sulfide (H_2S) is purged from the system into the wastewater blow-down.

See also: Biogas, Gas Cleaning, Gas Processing, Gas Treating.

Biogenic Coal Bed Methane

All coals contain biogenic gas, but only the higher rank coal (bituminous) contains thermogenic gas. Biogenic methane is formed in coal seams by naturally occurring bacteria that are associated with meteoric water recharge at outcrop or sub-crop. Biogenic methane is a term used to describe natural gas derived from the reduction of carbon dioxide via biogeochemical processes. The processes which contribute to the production are complex, poorly understood, but pervasive in nature and vary from site to site. Biological processes include methanogenesis and hydrogenogenesis, but there are also geochemical processes that have been identified. Methanogenic bacteria generate methane by several pathways, principally the fermentation of acetate and the reduction of carbon dioxide. In coal seams, methanogens may increase coalbed methane production.

See also: Biogas.

Biogeochemical Cycles

A biogeochemical cycle (also called the substance turnover or cycling of substances) is a pathway by which a chemical substance moves through biotic compartments (the biosphere) and through abiotic compartments of the Earth (such as the atmosphere, the hydrosphere, and the lithosphere).

There are biogeochemical cycles for the chemical elements (such as calcium, carbon, hydrogen, mercury, nitrogen, oxygen, phosphorus, selenium, and sulfur) as well as ; molecular cycles for water and silica; macroscopic cycles such as the rock cycle as well as human-induced cycles for synthetic compounds such as polychlorinated biphenyl derivatives (PCBs). In some cycles, there are *reservoirs* where a substance remains for a long period of time.

The biogeochemical cycles operate at the global scale and involve all of the main components of the Earth system in which materials are transferred continually between the atmosphere, the aquasphere, and the geosphere. However, since the biogeochemical cycles involve elements that are essential for life, organisms play a vital part in those cycles. Typically then, the biogeochemical cycles involve an inorganic component (the abiotic part of the cycle, including sedimentary and atmospheric phases) and an organic component (comprising plants and animals, both living and dead). Like other environmental systems, biogeochemical cycles involve the flow of substances between stores (also known as reservoirs) in the geosphere, atmosphere, hydrosphere, and biosphere. Water plays a vital role in mediating many of the flows between stores. Three of the key biogeochemical cycles are the nitrogen, carbon, and sulfur cycles.

Finally, it must be noted that the biogeochemical cycles have been modified substantially by human activities which is necessary for consideration to understand the various environmental issues related to human activities.

Biohydrogen

Biohydrogen is hydrogen produced biologically (by biological process), most commonly by bacteria from waste organic materials.

Hydrogen (H_2) is not available independently in the atmosphere, but is always combined with other elements. Hence, before being used, it has to be extracted from various compounds, e.g., via the syngas route. Currently, hydrogen is produced mainly from natural gas and to a lesser extent from oil derivatives (totally 77% of all hydrogen production), while its production from biomass is new – due partly to the more sophisticated manufacturing of syngas from biomass compared to natural gas, but also to the much lower relative hydrogen content of biomass vice-versa natural gas.

Hydrogen can be produced from biomass by pyrolysis, gasification, steam gasification, steam-reforming of bio-oils, and enzymatic decomposition of sugars. The yield of hydrogen that can be produced from biomass is relatively low, 16 to 18% based on dry biomass weight. In the pyrolysis and gasification processes, water-gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption is used to purify the product. Gasification coupled with water gas shift is the most widely practiced process route for biomass to hydrogen. In general, the gasification temperature is higher than that of pyrolysis and the yield of hydrogen from the gasification is higher than that of the pyrolysis. Modeling of biomass steam gasification to synthesis gas is a challenge because of the variability (composition, structure, reactivity, physical properties, etc.) of the raw material and because of the severe conditions (temperature, residence time, heating rate, etc.) required. Hydrogen can be produced via steam gasification of biomass materials. The yield of H_2 from steam gasification increases with increasing water-to-sample (W/S) ratio. The yields of hydrogen from steam gasification increase with increasing temperature.

Several concepts have promise for near-term to long-term process development for biohydrogen production. For example, the microbial shift reaction (analogous to one step of the steam methane reaction in coal gasification), operates at ambient temperatures in a single-stage process, compared to the two-stage, high-temperature, chemical catalyst processes currently used. Process development is just beginning, but this concept appears promising for near- to mid-term practical applications.

Hydrogen yields from the fermentation of organic wastes are typically less than 20% (on a heating value basis) compared to methane production. Higher yields might be possible at elevated temperatures, with nutrient limitations, and through metabolic engineering of the bacteria.

Photofermentation, the conversion of organic substrates to hydrogen by nitrogen-fixing photosynthetic bacteria, achieve high yields of hydrogen, but low solar conversion efficiencies. The inefficiency of the nitrogenase enzyme suggests that biohydrogen processes must be based on reversible hydrogenases.

Larger-scale biohydrogen production requires biophotolysis processes, such as hydrogen production from water and sunlight. Photobioreactor costs and solar conversion efficiencies are main challenges in the development of practical processes. Direct biophotolysis couples the reductant produced by photosynthesis directly to hydrogenase, producing oxygen and hydrogen simultaneously, while indirect processes separate these basically incompatible

reactions through intermediate carbon dioxide fixation. Direct, but not indirect, biophotolysis processes would require hydrogenase activity in the presence of high oxygen levels.

The photosynthetic production of hydrogen employs microorganisms such as cyanobacteria, which have been genetically modified to produce pure hydrogen rather than the metabolically relevant substances. The conversion efficiency from sunlight to hydrogen is small, usually under 0.1%, indicating the need for large collection areas. However, hydrogen build-up hinders further production and there has to be a continuous removal of the hydrogen produced, by pipelines to e.g., a shore location, where gas treatment and purification can take place.

Furthermore, if the bacteria are modified to produce maximum hydrogen, their own growth and reproduction are quenched. There presumably has to be a compromise made between the requirements of the organism and the amount of hydrogen produced for export, so that replacement of organisms (produced at some central biofactory) does not have to be made at frequent intervals.

Hybrid indirect processes using both algae and photosynthetic bacteria have been proposed and tested. The simplest indirect process would use the same algal cells for carbon dioxide fixation, oxygen evolution, and hydrogen production, at separate times or even in different reactors. The hydrogen reactions would take place both in the dark and light. Light-driven hydrogen evolution requires suppression of the oxygen evolution process. The biophotolysis process must achieve the highest possible solar conversion efficiencies, which will require development of algal strains with reduced light-harvesting pigment content.

See also: Biological Hydrogen Production, Hydrogen Production.

Biohydrogen – Production

The photosynthetic production of hydrogen employs microorganisms such as cyanobacteria, which have been genetically modified to produce pure hydrogen rather than the metabolically relevant substances. The conversion efficiency from sunlight to hydrogen is small, usually under 0.1%, indicating the need for large collection areas.

Hydrogen build-up hinders further production, and there has to be a continuous removal of the hydrogen produced, by pipelines to e.g., a shore location, where gas treatment and purification can take place. Furthermore, if the bacteria are modified to produce maximum hydrogen, their own growth and reproduction are quenched. There presumably has to be a compromise made between the requirements of the organism and the amount of hydrogen produced for export, so that replacement of organisms (produced at some central biofactory) does not have to be made at frequent intervals.

See also: Hydrogen.

Biological Action

Biological action is the action of biological organism on a substrate to produce a product, such as is envisioned in the production of biofuels by biological agents. In a scientific sense, a biological process is a method or means of changing one or more chemical reactions due to the activity of the biological agent which may result in a change in the composition of chemical(s) or material(s).

Although biological actions may involve only one step, often, multiple steps are involved. In the case of multiple steps, the steps may be sequential in time or sequential in space. Also, for a given amount of a feedstock, an expected amount of material can be determined at key steps in the process.

Thus, a biological process or bioconversion process involves the conversion of biomass into bioenergy, fertilizer, food, and chemicals through the biological action of microorganisms. One of the important biofuels obtained through bio-conversion is biogas (which is predominantly methane). In addition, and in the current context, biological processes are those processes that are vital for an organism to survive, and that shape the ability of the organism to interact with its environment. Biological processes involve many chemical reactions or other events that are involved in the persistence and transformation of life forms.

In contrast, the non-biological processes such as (a) direct combustion, (b) conversion of biomass into liquid fuels such as fuel oil (e.g., by pyrolysis - a type of fertilization, liquefaction, etc.), and (c) gasification.

See also: Bioconversion Platform, Biogas, Biohydrogen, Biological Conversion – Anaerobic Digestion.

Biological Alcohol

A biological alcohol is any alcohol that is provided through the action of a biological agent (such as a microbe, typically the biological agent is a colony of microbes) on a feedstock.

As an example, the fermentation process is a complex biochemical process during which yeast converts sugars to ethanol, carbon dioxide, and other metabolic by-products that contribute to the chemical composition and sensorial properties of the fermented foodstuffs. Control of the fermentation process is generally considered as a prerequisite to determine the quality of the final product. In this context, fermentation monitoring is a growing need, which calls for fast, low-cost, and nondestructive methods providing real-time or online information in order to assure an effective control at all stages of the process.

The production of the biological alcohol is accomplished by yeast, certain types of bacteria, as well as other microorganisms that result in the conversion of sugar derivatives into ethyl alcohol and carbon dioxide. In the process, yeast is mostly used as the biological agent and the yeast generally carries out the aerobic fermentation process, but it may also ferment the raw materials under anaerobic conditions. The process commences with the breakdown of sugars by yeasts to form pyruvate molecules (glycolysis) which, in the case of glucose, produces two molecules of pyruvic acid. The two molecules of pyruvic acid are then reduced to two molecules of ethanol and carbon dioxide.

Under anaerobic conditions, the pyruvate can be transformed to ethanol, where it first converts into an intermediate product (acetaldehyde, CH_3CHO) which further releases carbon dioxide and is converted into ethanol ($\text{CH}_3\text{CH}_2\text{OH}$).

See also: Bioalcohol, Bioethanol, Fermentation, Fermentation Chemistry.

Biological Conversion

Biological conversion (also referred to as biochemical conversion) involves breaking down biomass to make the carbohydrates available for processing into sugars, which can then be converted into biofuels and bioproducts through the use of microorganisms and catalysts. Potential fuel blend stocks and other bioproducts include the following: (i) renewable gasoline, (ii) ethanol and other alcohols, (iii) renewable chemical products, and (iv) renewable diesel.

Biochemical conversion uses biocatalysts, such as enzymes, in addition to heat and other chemicals, to convert the suitable portions of biomass (hemicellulose and cellulose) into an intermediate sugar stream. These sugars are intermediate building blocks that can then be fermented or chemically catalyzed into a range of advanced biofuels and value-added chemicals.

Bioconversion processes generally take place in bioreactors, which may be operated in batch, continuous, or semi-continuous mode, among others. Moreover, different bioreactor configurations may be suitable depending on the specific application. The technology may range from solid-phase bioconversion processes to gas-phase ones, besides aqueous phase bioprocesses. In any case, a given amount of moisture is generally needed, as this is required, in most cases, for optimal microbial activity. For any given feedstock, biocatalyst and bioreactor configuration and operating conditions will need to be optimized, in terms of aspects such as residence time in continuous processes, pH, or media composition (such as, for example, the carbon-nitrogen ratio).

Thus, bioconversion processes and biorefineries are environmentally friendly alternatives to common chemical processes and conventional oil refineries. They allow the production of a wide range of products with cheap biocatalysts, usually under mild conditions.

See also: Biohydrogen, Biological Action, Biological Alcohol.

Biological Conversion – Aerobic Digestion

Aerobic digestion is the biochemical oxidative stabilization of wastewater sludge in open or closed tanks that are separate from the liquid process system. Aerobic digestion is a solids stabilization process that provides a limited supply of oxygen to microorganisms in order to facilitate oxidation of organic matter and convert it into carbon dioxide and water. The microorganisms utilized in aerobic digestion processes are mesophilic facultative bacteria which mean they thrive in temperatures between 20 and 37°C (68 and 100°F) and live under aerobic (presence of oxygen), anoxic (no

oxygen but with presence of nitrates), and anaerobic (no presence of oxygen or nitrates) conditions. Thus, the aerobic digester operates on the principle that as the food is depleted, the microbes, the endogenous phase, and the cell tissue are aerobically oxidized to carbon dioxide, water, ammonium ions (NH_4^+), nitrite ions (NO_2^-), and nitrate ions (NO_3^-).

In general, aerobic digestion is a relatively simple process; there are many design and operational parameters such as temperature control, oxygen transfer and mixing, nitrification and denitrification, solids retention time, pH control, sludge loading characteristics, and tank configuration that must be considered in order to achieve a sustainable process.

Typically, an aerobic digestion system consists of two or more aerated tanks used to process and store waste-activated sludge generated from the liquid treatment process and/or primary sludge from primary sedimentation tanks. The waste-activated sludge and primary sludge in an aerobic digestion system can be processed separately or can be combined into one product. Air is introduced to the tank(s) from an aeration system typically coarse or fine bubble diffuser equipment with the air being supplied by a positive displacement or centrifugal blower.

The bacteria continue metabolism as they do in the liquid process, but without new food, they use their own biomass (endogenous respiration). This stabilizes the sludge so that it is safer for human contact, does not attract vermin (vectors), and odors are reduced. This method of digestion is capable of handling waste-activated, trickling filter, or primary sludges as well as mixtures of the same.

Biological Conversion – Anaerobic Digestion

Anaerobic digestion is the decomposition of biological wastes by microorganisms, usually under wet conditions, in the absence of air (oxygen), to produce a gas comprising mostly methane and carbon dioxide. A digester system (the anaerobic digester) is a device that promotes the decomposition of manure or digestion of the organics in manure to simple organics and gaseous biogas products.

During anaerobic digestion of an organic material such as biomass, a varied mixture of complex compounds is converted to a very narrow range of simple compounds, mainly methane and carbon dioxide. The anaerobic bacteria are responsible for the biochemical transformation of the biodegradable organic fraction (BOF). The AD of organic material basically consists of hydrolysis, acidogenesis, acetogenesis, and methanogenesis. These transformations are involved in the breakdown of complex polymers, such as cellulose, fats, and proteins to long and short chain fatty acids, and finally to methane, carbon dioxide, and water.

Any organic substance can become subject to anaerobic digestion so long as there are warm, wet, and airless conditions. For example, marsh gas is a product of the anaerobic digestion of vegetation at the bottom of ponds; this gas rises to the surface and bubbles, and the gas is also combustible. With the aid of human intervention, there are two products of this process, biogas and landfill gas. The chemical processes behind the production of these gases are complex.

The anaerobic digestion process focuses on hastening the natural process of biomass conversion to a gaseous fuel (biogas). Research has been conducted to ascertain optimal conditions for anaerobic digestion. These include (i) the feedstock, (ii) the nutrients, (iii) the temperature, (iv) the moisture content of the feedstock, (v) the pH of the system, and (vi) the atmospheric conditions. Most of the biomass waste feedstocks (municipal solid waste, agricultural waste, farm waste, crop waste, and forestry waste) studied have produced a biogas rich in methane. This medium to high Btu gas can, in some instances, be upgraded to a substitute natural gas (SNG). Depending on the feedstock, sulfur may also be produced.

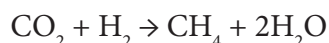
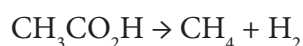
Anaerobic digestion is a multi-stage biological waste treatment process whereby bacteria, in the absence of oxygen, decompose organic matter to carbon dioxide, methane, and water. In this way, the waste sludge is stabilized and the obnoxious odor is removed. The process can, however, be described adequately and simply as occurring in two stages, involving two different types of bacteria. The process occurs in the absence of air; the decomposition in this case is caused not by heat but by bacterial action. In the first stage, the organic material present in the feed sludge is converted into organic acids (also called volatile fatty acids) by acid-forming bacteria. In the second stage, these organic acids serve as the substrate (food) for the strictly anaerobic methane-producing bacteria, which converts the acids into methane and carbon dioxide. The end result of the process is a well-established sludge in which 40 to 60% of the volatile solids are destroyed. Finally, a combustible gas is produced consisting of 60 to 75% methane and the remainder largely being carbon dioxide.

The anaerobic digestion process is a multi-stage biological waste treatment process whereby bacteria, in the absence of oxygen, decompose organic matter to carbon dioxide, methane and water. In this way, the waste sludge is stabilized and the obnoxious odor is removed. The process can, however be described adequately and simply as

occurring in two stages, involving two different types of bacteria. In the first stage, the organic material present in the feed sludge is converted into organic acids (also called volatile fatty acids) by acid-forming bacteria. In the second stage, these organic acids serve as the substrate (food) for the strictly anaerobic methane-producing bacteria, which converts the acids into methane and carbon dioxide. The end result of the process is a well-established sludge in which 40 to 60% v/v of the solids are consumed by the process. Finally, a combustible gas consisting of approximately 60 to 75% v/v methane is produced with the remainder being predominantly carbon dioxide.

Anaerobic digestion is a complex process which requires strict anaerobic conditions [oxidation reduction potential (ORP) < -200 mV] to proceed and depends on the coordinated activity of a complex microbial association to transform organic material into mostly carbon dioxide and methane. Despite the successive steps, hydrolysis is generally considered as rate limiting. The hydrolysis step degrades both insoluble organic material and high molecular weight compounds (lipids, polysaccharides, proteins, and nucleic acids) into soluble organic substances (amino acids and fatty acids). The components formed during hydrolysis are further split during acidogenesis, the second step.

Volatile fatty acids (VFAs) are produced by acidogenic bacteria along with ammonia (NH₃), carbon dioxide (CO₂), hydrogen sulfide (H₂S), and other by-products. The 3rd stage in anaerobic digestion is acetogenesis, where the higher organic acids and alcohols produced by acidogenesis are further digested by acetogens to produce mainly acetic acid and as well as carbon dioxide and hydrogen. The final stage of methanogenesis produces methane by two groups of methanogenic bacteria: (i) the first group splits acetate into methane and carbon dioxide and (ii) the second group uses hydrogen as an electron donor and carbon dioxide as the acceptor to produce methane. Thus:



The digestion process is continuous – fresh feedstock must be added continuously or at pre-determined frequent intervals. The gas formed during digestion is removed continuously. In high-rate digestion, stabilized sludge is displaced from the digester during feeding. In low-rate digestion, supernatant sludge is typically removed as the feed sludge is added; stabilized sludge is removed at less frequent intervals.

In a typical anaerobic digestion process, biomass is simply allowed to degrade in an anaerobic environment. A number of factors affect the entire process. They include (i) the temperature of the substrate, (ii) the loading rate, (iii) the pH, (iv) the residence time, (v) the concentration of nutrients, and (vi) the presence of any toxic substances.

In terms of temperature, the optimal temperature (where digestion and gasification proceeds at the highest rate) is 35°C (95°F). Below 15°C (59°F), the rate is so slow that little gas is produced. Temperature is also dependent on the bacterial populations: mesophilic or thermophilic. Mesophilic bacteria prefer temperatures ranging from 30 to 40°C. Thermophilic bacteria prefer temperatures ranging from 50 to 60°C (140°F).

The loading rate is the amount of fermentable matter that is fed into the digester per cubic meter of digester capacity. Any change in loading rate affects the balance inside the digester, so it should be kept constant. For a given capacity, if the loading rate is increased, the fermentation period is correspondingly increased. The common range of solid concentration is 7 to 9%, and digression from this range can cause fermentation to be retarded. In terms of the alkalinity/acidity (pH), the optimal gas formation occurs at pH of 7 to 8. If the pH becomes too acidic, gas production could stop altogether.

The retention time is the amount of time fermentable material resides inside the digester. It has been observed that maximum gas production takes place within the first four weeks, and then gradually tapers off. Detention time can be significantly reduced if the temperature is raised or the contents of the digester are agitated, or the supply of nutrients in the digester is augmented. Usually, some type of nutrient source is needed to help stimulate gas production. Bacteria use nitrogen, phosphorus, and potassium for their nutrients. Once these are available, fermentation proceeds very quickly. However, caution is advised that, although rare, toxic substances such as copper can inhibit gas production if found in large quantities.

It is essential that the organic acids formed in the first stage of the waste treatment process are converted to methane at the same rate at which they are formed. If not, they accumulate and ultimately lower the pH, leading to inhibition of the second stage of the digestion process and digester failure. The temperature must be maintained within certain ranges - heating increases the activity of the anaerobic bacteria reducing the required digestion time.

A pH of 7.0 to 7.5 is recommended to encourage the methane-producing stage. A correctly operating digester will have sufficient buffer capacity (alkalinity) introduced from the breakdown of organic matter. Also, the gas leaving the digester is almost saturated with water vapor which condenses as the gas stream cools there causing problems – the problem is more severe when digesters are heated. To mitigate the problem, it is essential to remove as much of the moisture as possible before the gas comes into contact with the gas system devices. For this reason, water traps should be located as close to the digester as possible and all piping should be sloped a minimum of 1% toward the water trap, which should be situated at a low point in the gas line.

Several types of digesters have been developed including the floating drum, the fixed dome, the bag, the plastic tube, the plug flow, and the up-flow anaerobic sludge blanket digesters. A digester is an airtight vessel or enclosure in which bacteria decomposes biomass in water to produce biogas. Both batch and continuous digesters are commercially available. While batch systems may be suitable for some applications, they are labor intensive, and in developed countries are probably not appropriate to the steady production of gas on any significant scale.

Mixing may be used in both batch and continuous digesters to enhance contact between the bacteria and substrate. It has, however, been argued that while mixing may increase conversion rates, it is not energy efficient. In two-stage systems, only the first stage is mixed. Multistage systems provide optimum conditions for the successive digestive steps, and further development may prove them to be economical for some biomass materials.

In a process of manure and straw mixture digestion, for the first 72 hours, the yield of methane was minimal (essentially 0%) and the yield of carbon dioxide is virtually quantitative (approximately 100%) – in this period, digestion occurred as aerobic fermentation to carbon dioxide. The yields of methane and carbon dioxide gases were approximately equal after 250 hours, and after 500 hours, the digestion reached the stationary phase. The methane content of the biogas was in the range of 73 to 79% for the runs, the remainder being principally carbon dioxide. During a 720-hour digestion period, approximately 80 to 85% v/v of the biogas was produced in the first 360 to 430 hours which is an indication that the digester retention time can be designed to a shorter period (360 to 430 hours) instead of the longer period (720 hours).

The final stage in the process is the disposal of the any waste. Essentially all the water entering the system will be present in the effluent. Direct recycle of the water after separation from the sludge cannot be practiced, as this will result in a buildup of toxic substances and eventual failure of the system. It is possible that some fraction of the water may be safely recycled, although data on this aspect have not been seen. Treatment of this large volume of water to remove the toxic constituents is costly and is likely to be uneconomical other than in large-scale operations.

Typically, it can be assumed that the water, which is considered to have some nutritional value, can be used for irrigation of growing crops. However, serious consideration must be given to the effect of trace metals and other toxic materials present in the water and the effects of these constituents on the crops. In addition, subject to the presence of non-toxic constituents (or the lack of toxic constituents) in the sludge, it also may be used for land application and will generally have higher nitrogen content than the original material. On an absolute (feedstock-to-sludge) basis, there may be less nitrogen retention due to losses of the nitrogen as ammonia (NH_3), and there may be additional losses on land application since the nitrogen in the sludge is in a more volatile form than the nitrogen in the original feedstock. Nevertheless, the sludge resulting from the digestion of animal manure is generally considered (subject to a critical analysis of the constituents of the sludge) to have improved fertilizer value over the original feedstock. During digestion, the volatile fatty acid concentration is lower and the pH higher. Nearly all digester plants have ancillary processes to treat and manage all of the by-products. Before storage and use, the gas stream is dried and sweetened by removal of sulfur compounds. The sludge liquor mixture has to be separated by one of a variety of ways, the most common of which is filtration. Excess water is also sometimes treated in sequencing batch reactors (SBR) for discharge into irrigation systems.

Essentially all organic material can be digested except for the stable woody materials since the anaerobic microorganisms are unable to degrade lignin. The biogas which is formed has a high calorific value (heat content) and is considered as a renewable energy source. The main disadvantages of this process are (i) the possible presence of volatile siloxanes in the biogas that can cause serious damage in the energy users' engine and boiler due to the formation of microcrystalline silica; and (ii) the increased concentration of heavy metals and various industrial organic chemicals in the residual sludge due to the significant reduction of the organic fraction during digestion, leaving the mineral and non-degradable fraction untouched.

Anaerobic digestion produces a clean and environmentally friendly fuel, although it contains carbon dioxide, water vapor, hydrogen, hydrogen sulfide, and siloxane derivatives (i.e., compounds having a molecular structure

based on a chain of alternate silicon and oxygen atoms, -O-Si-O-Si-, especially – as in silicone derivatives – with organic groups attached to the silicon atoms).

As a note of caution, a mixture of biogas (predominantly methane) and air can be explosive. Methane in concentrations of between 5% and 15% v/v in air is explosive, and air should not be allowed to enter the digester or gasholder. All piping and equipment must be sealed properly to prevent gas from escaping to the outside. In addition, all electrical installations must be of the explosion-proof type, as the smallest spark could ignite escaped gases.

Biomass feedstocks generally produce a biogas rich in methane. This medium-to-high Btu (heat content) gas can, in some instances, be upgraded to a substitute natural gas (SNG). However, depending on the feedstock, non-negligible amounts of sulfur are also produced (Table B-13).

Table B-13 Comparison of different biogas feedstocks.

Feedstock	Sulfur content*	Product sulfur*
Liquid and solid manure	300-500	0.5
Organic waste	100-300	0.3
Wood chips	300-1000	0.3
Sewage sludge	300-500	0.6

*mg/m³

See also: Anaerobic Digestion – Gas Production.

Biological Hydrogen Production

Biological hydrogen (biohydrogen) is hydrogen produced biologically. The main reactions involve fermentation of sugar derivatives, such as glucose:



A related reaction produces formic acid (leading to the potential for the production of formate derivatives (esters of formic acid) instead of carbon dioxide:



See also: Biohydrogen.

Biomass

Biomass refers to biological material derived from living or recently living organisms, such as plants or plant-derived materials. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel. Conversion of biomass to biofuel can be achieved by different methods, which are broadly classified into: (i) thermal, (ii) chemical, and (iii) biochemical methods. This biomass conversion can result in fuel in gas, liquid, or solid form.

Biomass is a renewable energy source unlike other resources such as crude oil, natural gas, tar sand, coal, and oil shale. Agricultural products specifically grown for biofuel production include crops such as corn, soybeans, rapeseed, wheat, sugar beet, sugar cane, palm oil, *Jatropha*, as well as wood (Table B-14).

Biomass is generally produced in a sustainable manner from water and carbon dioxide by photosynthesis. There are three main categories of biomass—primary, secondary, and tertiary.

Table B-14 Major categories of biomass feedstocks.

Algae	Prokaryotic algae, Eukaryotic algae, Kelps
Aquatic plants	Algae, Water weed, Water hyacinth, Reed and rushes
Biorenewable wastes	Agricultural wastes, Crop residues, Mill wood wastes, Urban wood wastes, Urban organic wastes
Energy crops	Short rotation woody crops, Herbaceous woody crops, Grasses, Starch crops, Sugar crops, Forage crops, Oilseed crops, Switchgrass, Miscanthus
Food crops	Grains, Oil crops
Forest products	Wood; Logging residues; Trees, shrubs, and wood residues; Sawdust, bark etc.
Landfill	Hazardous waste, Non-hazardous waste, Inert waste, Liquid waste
Lichens	Crustose lichens, Foliose lichens, Fruticose lichen
Mosses	Bryophyta, Polytrichales
Organic waste	Municipal solid waste, Industrial organic wastes, Municipal sewage, and sludge

Biomass is biological organic matter but is more often used to refer to (i) energy crops grown specifically to be used as fuel, such as fast-growing trees or switch grass, (ii) agricultural residues and by-products, such as straw, sugarcane fiber, and rice hulls, and (iii) residues from forestry, construction, and other wood-processing industries.

Many different types of biomass can be grown for the express purpose of energy production (Table B-15).

Table B-15 Sources, processing options, and uses of biomass-derived products*.

Resources	Collection	Conversion	End products
Stage 1	Stage 2	Stage 3	Stage 4
Agricultural crops			
Energy crops			
Forestry			
Herbaceous plants			
Oil-bearing plants			
Wastes			
	Harvesting		
	Handling		
		Pretreatment	
		Biochemical processes	
		Chemical processes	
		Physical processes	
		Thermochemical	
			Biodiesel
			Electrical power
			Heat
			Solid fuels
			Transportation fuels

*The sub-categories are listed alphabetically and are not listed in an order of preference for processing. The choice of processing preference is dependent upon the type of biomass and the desired product.

Crops that have been used for energy include sugar cane, corn, sugar beets, grains, elephant grass, kelp (seaweed), and many others. There are two main factors which determine whether a crop is suitable for energy use. Good energy crops have a high yield of dry material per unit of land (dry tonnes/hectare). A high yield reduces land requirements and lowers the cost of producing energy from biomass. Similarly, the amount of energy which can be produced from a biomass crop must be less than the amount of energy required to grow the crop. In some circumstances like the heavily mechanized corn farms in the U.S. Midwest, the amount of ethanol which can be recovered from the corn is barely larger than the fuel required for tractors, fertilizers, and processing.

The components of biomass include triglycerides, sterols, alkaloids, resins, terpenes, terpenoids, and waxes. This includes everything from primary sources of crops and residues harvested/collected directly from the land to secondary sources such as sawmill residuals, to tertiary sources of post-consumer residuals that often end up in landfills. A fourth source, although not usually categorized as such, includes the gases that result from anaerobic digestion of animal manures or organic materials in landfills.

Primary biomass is produced directly by photosynthesis and includes all terrestrial plants now used for food, feed, fiber, and fuel wood. All plants in natural and conservation areas (as well as algae and other aquatic plants growing in ponds, lakes, oceans, or artificial ponds and bioreactors) are also considered primary biomass. However, only a small portion of the primary biomass produced will ever be harvested as feedstock material for the production of bioenergy and by-products.

Biomass feedstocks and fuels exhibit a wide range of physical and chemical properties (Table B-16).

Table B-16 Selected properties of representative biomass materials.

Mass %, dry	Wood	Grain*	Municipal Solid Waste**	Animal Wastes (Manure)
Carbon	50-53	45.0	47.6	35.1
Hydrogen	5.8-7.0	5.8	6.0	5.3
Nitrogen	0-0.3	2.4	1.2	2.5
Sulfur	0-0.1	0	0.3	0.4
Oxygen	38-44	42.5	32.9	38.7
Volatile matter	77-87	70-80	77	76.5
Fixed carbon	13-21	—	11	0
Ash	0.1-2.0	4.0	12	23.5
H/C atom ratio	1.4-1.6	1.5	1.5	1.8
GCV, MJ/kg (dry)	19.8-21.0	16.8	19	13.4
Moisture, %	25-60	16	20	7-35

* Red corn cob (corn stover) contains approximately 25% cellulose, 10% lignin, and 15% moisture.

** Combustible portion; may contain 9% metals and 12% glass/ceramics on an as-received basis.

For example, there are many types of coal and the gross heating value of these types varies from 8,600-12,900 Btu/lb. However, nearly all kinds of biomass feedstocks destined for combustion range from 6,450 to 8,200 Btu/lb. For most agricultural residues, the heating values are even more uniform – approximately 6,450 to 7,300 Btu/lb; the values for most woody materials are 7,750 to 8,200 Btu/lb. Moisture content is probably the most important determinant of heating value. Air-dried biomass typically has approximately 15 to 20% moisture, whereas the moisture content for oven-dried biomass is around 0%. Moisture content is also an important characteristic of coals, varying in the range of 2 to 30%. However, the bulk density (and hence energy density) of most biomass feedstocks is generally low, even after densification, approximately 10 and 40% of the bulk density of most fossil fuels. Liquid biofuels have comparable bulk densities to fossil fuels.

Combustion offers the most direct route for energy recovery from biomass, and is an effective means of utilizing the total energy content of whole wood and other biomass. Technology for small-scale combustion is certainly well

developed. Larger-scale operation for electricity generation at the 5 to 50 MW level should be feasible, although it is not expected to be economically competitive with crude oil- or natural-gas-fired systems. Due to the large land area over which wood must be harvested, the seasonal nature of the supply, and the large volume of material to be transported and stored, the reliable provision of wood to a large plant can present considerable problems.

Biofuels are derived from biomass and have the potential to produce fuels that are more environmentally benign than crude oil-based fuels. In addition, ethanol, a crop-based fuel alcohol, adds oxygen to gasoline thereby helping to improve vehicle performance and reduce air pollution. Biodiesel, an alternative or additive to crude oil diesel, is a nontoxic, renewable resource created from soybean or other oil crops.

Direct biofuels are biofuels that can be used in existing unmodified crude oil engines. Because engine technology changes all the time, direct biofuel can be hard to define; a fuel that works well in one unmodified engine may not work in another. In general, newer engines are more sensitive to fuel than older engines, but new engines are also likely to be designed with some amount of biofuel in mind.

See also: Biofuels.

Biomass Ash

The mineral matter in biomass is reflected in the yield of mineral ash that is produced during combustion of the biomass. Biomass ash is naturally alkaline. The mineral matter content of wood is small wood but can be as high as 20% w/w for some types of biomass. The alkali nature of ash tends to lower the fusion point of the ash thereby leading to fouling and slagging. An increase in the ash content can also arise from the presence of non-indigenous contaminants such as soil, rocks, plastic, metals, and various chemical treatments of the biomass. Those contaminants can lead to severe problems like pollutant formation, fouling, and slagging.

Biomass with high content of alkali (and chlorine) has often caused problems with the formation of deposits and corrosion. Using additives rich in silicon, aluminum, calcium, potassium, sulfur, or calcium can reduce these problems.

Slagging in combustion units is caused by molten ash and is one of the main drawbacks with using biomass fuels, especially when waste biomass fuels originating from industry or agricultural production are used. The problems are caused by the typically higher content of mineral matter in these fuels but also due to the typically lower ash melting temperatures compared to fossil fuels or pure wood.

The key technical ash-related problems encountered by operators of biomass combustors and boilers have been associated with (i) the formation of fused or partly fused agglomerates and slag deposits at high temperatures within furnaces and stoves, (ii) the formation of bonded ash deposits and accumulations of ash materials at lower temperatures on surfaces in the convective sections of boilers, (iii) the accelerated metal wastage of furnace and boiler components due to gas-side corrosion under ash deposits, and due to ash-particle impact erosion or ash abrasion of boiler components and other equipment, (iv) the formation and emission of sub-micron aerosols and fumes, (v) the effect of biomass ash on the performance of flue gas cleaning equipment, and (vi) the handling, utilization, and disposal of ash residues from biomass combustion plants and mixed ash residues from the co-firing of biomass in coal-fired boilers.

Currently, there are solutions for combusting fuels with lower ash melting temperatures, such as wheat straw, but they have to be adapted specifically to a specific quality of the fuel. Fuel quality, however, varies widely between different types of biomass and biomass waste and can also vary with the season and especially during the handling of the fuel, which can cause contamination with soil, dirt, or other waste materials.

For biomass gasification and pyrolysis systems, the ash-related issues are largely similar to those for combustion, i.e., the accumulation of ash material within the reactor and associated equipment, the effect of ash on the integrity of the process plant and heat exchangers and the ash-related environmental effects of the process.

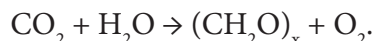
See also: Ash.

Biomass Chemistry

Biomass is typically composed of 75 to 90% by weight sugar species, the other 10 to 25 wt% being mainly lignin. The energy in biomass is the chemical energy associated with the carbon and hydrogen atoms contained in oxidizable

organic compounds which are the source of the carbon and hydrogen is carbon dioxide and water. The conversion by plants of carbon dioxide and water to a combustible organic form occurs by the process of photosynthesis in which solar energy and chlorophyll are the important players.

Chlorophyll, present in the cells of green plants, absorbs solar energy and makes it available for the photosynthesis, which may be represented by the simplified chemical reaction:



The oxidizable organic materials that are produced by photosynthesis and which determine the properties of the plant matter of relevance to biomass energy utilization are carbohydrates and lignin.

All of the carbohydrates present are saccharides (i.e., sugars) or polymers of sugars (i.e., polysaccharides) that fall into three types: (i) starch, (ii) cellulose, and (iii) hemicellulose. The simple sugars include glucose, fructose, and the like, while the polymeric sugars such as cellulose and starch can be readily broken down to their constituent monomers by hydrolysis, preparatory to conversion to ethanol or other chemicals.

Starch is a granular polysaccharide which accumulates in the storage tissues of plants such as seeds, tubers, roots, and stem pith. It is an important constituent of corn, potato, rice, and tapioca. Starch consists of 10 to 20% amylose, which is water soluble, and 80 to 90% amylopectin, which is insoluble. Both the constituents of starch are polymers of glucose, with amylose linked in chain structures, while amylopectin is a highly branched structure. Starch is not as chemically resistant as cellulose, and can be readily hydrolyzed by dilute acids and enzymes to fermentable sugars.

Hemicelluloses are polysaccharides that occur in association with cellulose. They are chemically different from cellulose, are amorphous, and have much lower molecular weight mass. While cellulose is built from the single sugar glucose, most hemicelluloses contain two to four different sugars as building blocks. Glucose is a component of some hemicelluloses, although xylose is a dominant sugar in hardwood hemicellulose, and mannose is important in softwood hemicellulose. Unlike the other sugars described so far, xylose contains only 5 carbon atoms and is a pentose.

The fraction of the cellulose containing xylose polymers is often referred to as pentosan. Hemicellulose is more soluble than cellulose, is dissolved by dilute alkaline solutions, and can be relatively readily hydrolyzed to fermentable sugars.

In contrast, lignin is a complex structure containing aromatic groups and is less readily degraded. Although lignocellulose is one of the cheapest and most abundant forms of biomass, it is difficult to convert this relatively unreactive material into sugars. Among other factors, the walls of lignocellulose are composed of lignin, which must be broken down in order to render the cellulose and hemicellulose accessible to acid hydrolysis. For this reason, many programs focused on ethanol production from biomass are based almost entirely on the fermentation of sugars derived from the starch in corn grain.

Lignin is the final major constituent of plant material important to biomass processing, and it is a complex chemical compound that is most commonly derived from wood and is an integral part of the cell walls of plants. The chemical structure of lignin is unknown and, at best, can only be represented by a hypothetical formula, the veracity of which is questionable. In fact, lignin is one of most abundant organic compounds on earth after cellulose and chitin.

By way of clarification, chitin ($\text{C}_8\text{H}_{13}\text{O}_5\text{N})_n$ is a long-chain polymeric polysaccharide of β -glucose that forms a hard, semitransparent material found throughout the natural world. Chitin is the main component of the cell walls of fungi and is also a major component of the exoskeletons of arthropods, such as the crustaceans (e.g., crab, lobster, and shrimp), and the insects (e.g., ants, beetles, and butterflies), and of the beaks of cephalopods (e.g., squids and octopuses).

Like hemicellulose, lignin is amorphous and more soluble than cellulose. It may be removed from wood by steaming or by dissolving in hot aqueous or aqueous bisulfite solution. Lignin resists hydrolysis and is resistant to microbial degradation.

Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components and is covalently linked to hemicellulose. Lignin also forms covalent bonds to polysaccharides and thereby cross-links different plant polysaccharides. It confers mechanical strength to the cell wall (stabilizing the mature cell wall) and therefore the entire plant.

See also: Hemicellulose, Lignin, Starch.

Biomass Combustion

Combustion is widely used on various scales to convert biomass energy to heat and/or electricity with the help of a steam cycle (stoves, boilers, power plants). Production of heat, power, and (process) steam by means of combustion is applied for a wide variety of fuels, and from small scale (for domestic heating) to a scale in the range of 100 MWe. Co-combustion of biomass in (large and efficient) coal-fired power plants is an especially attractive option as well because of the high conversion efficiency of these plants. It is a proven technology, although further improvements in performance are still possible.

Net electrical efficiencies for biomass combustion power plants range from 20 to 40%. The higher efficiencies are obtained with systems over 100 MW_e or when the biomass is co-combusted in coal-fired power plants.

See also: Biomass – Direct Combustion.

Biomass Composition and Properties

Biomass is a term used to describe any material of recent biological origin, including plant materials such as trees, grasses, agricultural crops, and even animal manure. The bulk composition (in terms of the amounts of cellulose, hemicellulose, and lignin) is, as might be expected variable opening upon the source and types of the biomass (Table B-17).

Table B-17 Bulk composition of different biomass type (% w/w, dry basis).

Biomass type	Cellulose	Hemicellulose	Lignin
Peat	10	32	44
Rice husks	30	25	12
Straw (wheat)	40	28	17
Wood (bark)	34	16	34
Wood (hard)	39	35	20
Wood (soft)	41	24	28

The elemental composition also shows some variation with the source of the biomass (Table B-18).

Table B-18 Elemental composition, ash production, and heat content of biomass types*.

Biomass, % w/w**	C	H	N	O	Ash
Miscanthus	49.5	6.2	0.6	43.7	3.3
Peat	53.1	5.5	1.3	38.1	5.6
Reed grass	49.4	6.3	1.6	42.7	8.8
Straw (wheat)	49.6	6.2	0.6	43.6	4.7
Sugar cane	49.5	6.2	0.5	43.8	3.7
Wood (bark)	47.2	5.6	0.3	46.9	3.9
Wood (birch)	48.8	6.0	0.5	44.2	0.5
Wood (pine)	49.3	6.0	0.5	44.2	0.5

*Listed alphabetical rather than by any preference.

**Dry basis

The obvious data are those relating to the amount of oxygen in the biomass which will require (at some stage of the refining) a hydrodeoxygenation step.

In terms of the bulk composition, other biomass components, which are generally present in minor amounts, include (i) triglyceride derivatives, which are ester derivatives of glycerol three fatty acids, (ii) sterol derivatives, which are also known as steroid alcohol derivatives), (iii) alkaloid derivatives, which form a class of naturally occurring organic compounds that mostly contain basic nitrogen atoms, (iv) terpene derivatives, which are the primary constituents of the essential oils of many types of plants and flowers, (v) terpenoid derivatives, which are sometimes referred to as isoprenoids and form a large and diverse class of naturally occurring organic chemicals derived from terpenes – most are multicyclic structures with oxygen-containing functional groups), and (vi) wax derivatives, which are a diverse class of organic compounds that are lipophilic, malleable solids near ambient temperatures and include higher molecular weight alkane derivatives and lipids, typically with melting points above approximately 40°C (104°F) and melt to give low-viscosity liquids. Waxes are insoluble in water but soluble in organic, nonpolar solvents. Natural waxes of different types are produced by plants and animals and occur in crude oil).

This list (above) includes everything from primary sources of crops and residues harvested/collected directly from the land, to secondary sources such as sawmill residuals, to tertiary sources of post-consumer residuals that often end up in landfills. A fourth source, although not usually categorized as such, includes the gases that result from anaerobic digestion of animal manures or organic materials in landfills (Wright et al., 2006).

Thus, knowledge of the composition of a biomass feedstocks is critical to the selection of the varieties with optimized properties for downstream conversion (De Jong, 2014). This can be partially achieved by selecting varieties with biomass composition that are better suited to the conversion process. Lignocellulosic biomass displays considerable recalcitrance to biochemical conversion because of the inaccessibility of its polymer components to enzymatic digestion and the release or production of fermentation inhibitors during pretreatment. If the ratio of hemicellulose, cellulose, and lignin in a woody biomass feedstock was optimized for the specific biochemical conversion method, then the pretreatment methods could be reduced or avoided.

Plants use the light energy from the sun to convert water and carbon dioxide to sugar derivatives (photosynthesis) that can be stored within the plant system. Some plants, such as sugar cane and sugar beets, store energy as simple sugars, while other plants store the energy as more complex starch derivative. These plants include grains like corn which are prominent food sources. Another type of plant matter – cellulosic biomass – is composed of complex sugar polymers, and is not generally used as a food source. Cellulosic feedstocks under consideration for biofuels include (i) agricultural residues which is the leftover material from crops, such as the stalks, leaves, and husks of corn plants, (ii) forestry wastes, which include chips and sawdust from lumber mills, dead trees, and tree branches, (iii) municipal solid waste, which includes household garbage and paper products, (iv) food processing and other industrial wastes such as black liquor, which is a paper manufacturing by-product (Table B-19), and (v) energy crops, such as fast-growing trees and grasses) developed just for this purpose.

Table B-19 Composition of black liquor.

Element	% w/w
Carbon	35.7
Hydrogen	3.7
Nitrogen	≥0.1
Oxygen	35.8
Sulfur	4.4
Chlorine	0.3
Potassium	1.1
Sodium	19.0

The main components of these types of biomass are (i) cellulose which is the most common form of carbon in biomass, accounting for 40 to 60% w/w of the biomass, depending on the biomass source and which is a complex sugar polymer, or polysaccharide, made from the six-carbon sugar, glucose – the crystalline structure of cellulose

renders it resistant to hydrolysis, the chemical reaction that releases simple, fermentable sugars from a polysaccharide; (ii) hemicellulose which is also a major source of carbon in biomass, at levels of between 20% and 40% w/w of the biomass and is a complex polysaccharide made from a variety of five-carbon and six-carbon sugar derivative – it is relatively easy to hydrolyze into simple sugars, but the sugars can be difficult to ferment, and (iii) lignin which is a complex polymer that makes up 10% to 24% w/w of the biomass and provides structural integrity in plants – it remains as residual material after the sugars in the biomass have been converted.

In the simplest sense, biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth, and heavy metals. However, because of the wide variations in the character and properties of biomass, it is anticipated and realized that the character and properties of the biofuels produced from biomass are very dependent upon the initial biomass. The exception is the fuels produced by gasification and Fischer-Tropsch synthesis.

In addition to the chemical composition, three properties of biomass that are significant to the performance of biomass as a fuel are (i) mineral matter content, manifested in thermal processes as mineral ash, (ii) susceptibility of the mineral matter to slagging and fouling, and (iii) the volatile matter content. The mineral matter content is the mass fraction of biomass composed of non-combustible inorganic material. Grasses, bark, and field crop residues typically have much higher content of mineral matter than wood. Systems that are designed to combust wood can be overwhelmed by the volume of ash if other biofuels are used. Slagging and fouling are problems that occur if ash begins to melt during combustion, forming deposits on combustor surfaces (fouling) or leaving hard chunks of glassy material in the bottom of the combustion chamber (slag, often referred to as clinkers).

Certain mineral components in biomass fuels, primarily silica, potassium, and chlorine, can cause these problems to occur at lower temperatures than normal. Dirt contamination also adds to the mineral content and associated slagging and fouling problems, so it is important that biomass feedstock be as clean (dirt-free) as possible. Slagging and fouling is minimized by keeping combustion temperatures low. Alternately, some biomass combustion equipment is designed to encourage the formation of clinkers (often referred to in the singular form, clinker) but is able to dispose of the hardened ash in an effective manner.

The content of volatile constituents (or volatile matter) in a fuel is a lesser-known property that refers to the fraction of the fuel that will readily volatilize (turn to gas) when heated to a high temperature. Fuels with high volatiles content will tend to vaporize before combusting, whereas fuels with low volatiles will burn primarily char. This affects the performance of the combustion chamber and should be taken into account when designing a combustor.

Other properties such as the particle size and density of biomass fuels are also important as they affect the thermal processing characteristics (especially the combustion characteristics) of biomass, especially the rate of heating and drying during the thermal process. The feedstock particle size also dictates the type of handling equipment required. For example, the incorrect size fuel will negatively impact process efficiency and may cause jamming or damage to the handling equipment. Smaller-sized fuel is more common for commercial-scale systems because smaller fuel is easier to use in automatic feed systems and allows for finer control of the processing rate by controlling the rate at which fuel is added to the reaction chamber. Fuel particle size and density are probably the most overlooked factors affecting fuel performance and should be given careful consideration when selecting a fuel type. Bulk density is the mass of a material divided by the volume it occupies. Bulk density of granular materials is dependent on the manner in which it is handled insofar as freely settled material has a lower bulk density than tapped or compacted materials.

Biomass – Conversion Technologies

There are many bioenergy routes which can be used to convert raw biomass feedstock into a final energy product. Several conversion technologies have been developed that are adapted to the different physical nature and chemical composition of the feedstock, and to the energy service required (heat, power, transport fuel). Upgrading technologies for biomass feedstocks (e.g., pelletization, torrefaction, and pyrolysis) are being developed to convert bulky raw biomass into denser and more practical energy carriers for more efficient transport, storage, and convenient use in subsequent conversion processes.

The production of heat by the direct combustion of biomass is the leading bioenergy application throughout the world and is often cost-competitive with fossil fuel alternatives. Technologies range from rudimentary stoves to sophisticated modern appliances. For a more energy-efficient use of the biomass resource, modern, large-scale heat applications are often combined with electricity production in combined heat and power (CHP) systems.

Different technologies exist or are being developed to produce electricity from biomass. Co-combustion (also called co-firing) in coal-based power plants is the most cost-effective use of biomass for power generation. Dedicated biomass combustion plants, including MSW combustion plants, are also in successful commercial operation, and many are industrial or district heating CHP facilities. For sludges, liquids, and wet organic materials, anaerobic digestion is currently the best-suited option for producing electricity and/or heat from biomass, although its economic case relies heavily on the availability of low-cost feedstock. All these technologies are well established and commercially available.

There are few examples of commercial gasification plants, and the deployment of this technology is affected by its complexity and cost. In the longer term, if reliable and cost-effective operation can be more widely demonstrated, gasification promises greater efficiency, better economics at both small- and large-scale and lower emissions compared with other biomass-based power generation options. Other technologies (such as Organic Rankine Cycle and Stirling engines) are currently in the demonstration stage and could prove economically viable in a range of small-scale applications, especially for CHP.

In the transport sector, first-generation biofuels are widely deployed in several countries – mainly bioethanol from starch and sugar crops and biodiesel from oil crops and residual oils and fats. Production costs of current biofuels vary significantly depending on the feedstock used (and their volatile prices), and on the scale of the plant. The potential for further deploying these first-generation technologies is high, subject to sustainable land use criteria being met.

First-generation biofuels face both social and environmental challenges, largely because they use food crops which could lead to food price increases and possibly indirect land use change. While such risks can be mitigated by regulation and sustainability assurance and certification, technology development is also advancing for next-generation processes that rely on non-food biomass (e.g., lignocellulosic feedstocks such as organic wastes, forestry residues, high-yielding woody or grass energy crops, and algae). The use of these feedstocks for second-generation biofuel production would significantly decrease the potential pressure on land use, improve greenhouse gas emission reductions when compared to some first-generation biofuels, and result in lower environmental and social risk.

Second-generation technologies, mainly using lignocellulosic feedstocks for the production of ethanol, synthetic diesel, and aviation fuels, are still immature and need further development and investment to demonstrate reliable operation at commercial scale and to achieve cost reductions through scale-up and replication. The current level of activity in the area indicates that these routes are likely to become commercial over the next decade. Future generations of biofuels, such as oils produced from algae, are at the applied R&D stage, and require considerable development before they can become competitive contributors to the energy markets.

Further development of bioenergy technologies is needed mainly to improve the efficiency, reliability, and sustainability of bioenergy chains. In the heat sector, improvement would lead to cleaner, more reliable systems linked to higher quality fuel supplies. In the electricity sector, the development of smaller and more cost-effective electricity or CHP systems could better match local resource availability. In the transport sector, improvements could lead to higher quality and more sustainable biofuels.

Ultimately, bioenergy production may increasingly occur in biorefineries where transport biofuels, power, heat, chemicals, and other marketable products could all be co-produced from a mix of biomass feedstocks. The link between producing energy and other materials deserves further attention technically and commercially.

Biomass-Derived Carbon

Biomass plays a unique role in the dynamics of carbon flow in the biosphere. Carbon is biologically cycled when plants such as soybean crops convert atmospheric carbon dioxide to carbon-based compounds through photosynthesis. This carbon is eventually returned to the atmosphere as organisms consume the biological carbon compounds and respire. Biomass-derived fuels reduce the net atmospheric carbon in two ways.

First, they participate in the relatively rapid biological cycling of carbon to the atmosphere (via engine tailpipe emissions) and from the atmosphere (via photosynthesis). Second, they displace fossil fuels. Fossil fuel combustion releases carbon that took millions of years to be removed from the atmosphere; combustion of biomass fuels participates in a process that allows carbon dioxide to be rapidly recycled to fuel. The net effect of shifting from fossil fuels to biomass-derived fuels is thus to reduce the amount of carbon dioxide in the atmosphere.

Because of the differences in the dynamics of fossil carbon flow and biomass carbon flow to and from the atmosphere, biomass carbon is often accounted for separately from carbon derived from fossil fuels.

See also: Biomass, Biomass – Pyrolysis.

Biomass – Direct Combustion

Direct combustion of biomass is a thermochemical technique in which the biomass is burned (combusted) in open air or in the presence of excess air. In this process, the photosynthetically stored chemical energy of the biomass will be converted into gases, unless char is also produced.

There are five thermal approaches that are commonly used to convert biomass into a renewable fuel: direct combustion, gasification, liquefaction, pyrolysis, and partial oxidation.

When biomass is heated under oxygen-deficient conditions, it generates synthesis gas that consists primarily of hydrogen and carbon monoxide. This syngas can be directly burned or further processed for other gaseous or liquid products. In this sense, thermal or chemical conversion of biomass is similar to that of coal.

Indoor direct combustion of biomass fuels in unvented cooking and heating spaces has caused considerable health problems to the direct users, primarily the women and children of developing countries. Biomass fuels, when used improperly in this manner, release considerable amounts of toxic or hazardous gases into the unvented area. These gases are typically: carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbon derivatives, organics, aldehydes, and trace amounts of aromatics and ketones. As the moisture content of the wood increases, and as other biomass fuels of lower energy content (such as animal and crop waste) are used, the emissions increase.

When the direct combustion of biomass is conducted in a well-ventilated area, biomass burning used for domestic stoves and boilers can be a sound substitute for combustion of conventional fossil fuel.

Most electrical power generation systems are relatively inefficient, due to the loss of a significant portion of energy, as much as half to two-thirds, in a form of waste heat. If this heat is used efficiently for industrial manufacture, space heating, district heating, or other purposes, the overall efficiency can be greatly enhanced. Therefore, smaller bio-power systems are more suitable for cogeneration type of processes than much larger counterparts.

See also: Biomass, Biomass-Chemistry, Biomass – Combustion, Biomass – Gasification, Biomass – Liquefaction, Biomass – Pyrolysis.

Biomass – Drying

Biomass with a high moisture content such as sludge is often used as fuel in power plant without proper drying which reduces the efficiency of the boiler. However, by use of a drying process, moisture can be largely removed from biomass. The result is a reduction in the weight of the biomass. This leads to a reduction of the processing costs, as well as of the costs for storage and transport. The dried end product is frequently used as a plant nutrient or it can be used as a fuel. This, however, depends on the properties of the biomass that needs to be dried.

Using dry fuel in a direct combustion boiler results in (i) improved efficiency, (ii) increased steam production, (iii) reduced ancillary power requirements, (iv) reduced fuel use, (v) lower emissions, and (vi) improved boiler operation. One of the main reasons for these benefits is an increased flame temperature. With wet fuel, some heat of combustion is used to evaporate the water in the fuel. With dry fuel, all the heat of combustion goes into heating the air and products of combustion. As a result, dry fuels have a flame temperature on the order of 1,260 to 1,370°C (2,300 to 2,500°F), while green wood has a combustion temperature of approximately 980°C (1,800°F). In cold climates, the heat of fusion of any ice that may be mixed with the fuel will also have a significant effect on the flame temperature.

Dryers can be broadly divided into two categories based on how heat is provided for drying. In direct dryers, the material gets heat from direct contact with a fluid providing the heat – either hot air or hot steam. With indirect drying, the material being dried is separated from the heat source by a heat exchange surface.

Directly heated dryers can be further divided into two more categories: air and superheated steam dryers (SSDs). In air dryers, hot air is contacted with the material to be dried. The air loses its sensible heat and provides the latent heat of evaporation to dry the material. The air also removes the water vapor that is evaporated. The material can be agitated by some mechanical means or by the flowing air.

In superheated steam dryers, the heating fluid is steam rather than air, but the concept is the same. The superheated steam is contacted with the biomass material and loses some of its sensible heat to provide the latent heat of evaporation to dry the fuel. The steam, however, remains above its saturation temperature, so it doesn't condense. The water vapor leaving the biomass is heated by the superheated steam, so the net result is a larger amount of steam at a lower temperature than when the steam entered the dryer. The excess steam is removed, and the remainder is reheated and recycled back to the dryer.

In the case of the indirectly heated dryer operated under a vacuum, or with a superheated steam dryer, the latent heat of evaporation of the water vapor is easy to recover because it is not diluted by air. With vacuum drying, this heat is available only at a low temperature, but with superheated steam drying, the dryer can be designed to produce steam at practically any pressure for use in other parts of the plant.

There are several steps to drying. First, the material must be heated from the temperature at which it entered the dryer, up to the wet bulb temperature, to produce a driving force for water to leave the wet material. Next, any surface moisture on the material is evaporated – this occurs fairly quickly. Once all the surface moisture is removed, the material must be heated to drive water from the inside of the biomass to the surface so it can evaporate. This occurs during the “falling rate period” when the rate of drying drops as the material becomes drier. During the falling rate period, the surface temperature of the material remains close to the wet bulb temperature. Once the material is completely dry, it begins to heat up to the surrounding temperature, because water is no longer present to keep the temperature low.

Rotary Dryers

Rotary dryers are the most common type for biomass. There are several variations of rotary dryers, but the most widely used is the directly heated single-pass rotary dryer. In this type of dryer, hot gases are contacted with biomass material inside a rotating drum. The rotation of the drum, with the aid of flights, lifts the solids in the dryer so they tumble through the hot gas, promoting better heat and mass transfer. If contamination is not a concern, hot flue gas can be fed directly into the dryer. Other options include using a burner or a steam heater to raise the temperature of incoming air.

The exhaust gases leaving the dryer may pass through a cyclone, multicyclone, baghouse filter, scrubber, or electrostatic precipitator (ESP) to remove any fine material entrained in the air. An air fan may not be required depending on the dryer configuration. If one is needed, it is usually placed after the emissions control equipment to reduce erosion of the fan, but may also be placed before the first cyclone to provide the pressure drop through downstream equipment.

The inlet gas temperature to rotary biomass dryers can vary from 232 to 1,095°C (450 to 2,000°F). Outlet temperatures from rotary dryers vary from 70 to 110°C (160 to 230°F) with most of the dryers having outlet temperatures higher than 104°C (220°F) to prevent condensation of acids and resins. Retention times in the dryer can be less than a minute for small particles and 10 to 30 minutes for larger material.

Flash Dryers

In a flash or pneumatic dryer, the solids are mixed with a high-velocity hot air stream. The intimate contact of the solids with the air results in very rapid drying. The solids and air are separated using a cyclone, and the gases continue through a scrubber to remove any entrained particulate material.

Gas temperatures are slightly lower for flash dryers than for rotary dryers, but they still operate at temperatures above the combustion point. The solids retention time in a flash dryer is typically less than 30 seconds, minimizing the fire hazard.

Disk Dryers

For smaller flows of material, a disk dryer or “porcupine” dryer (Figure 3) is an option. In a disk dryer, solids are heated by condensing steam inside of a central shaft with many hollow disks that increase the area for heat transfer. Fingers or breaker bars mix the material and act to keep the heat transfer surfaces free of buildup. The disk dryer can be operated under a vacuum or under pressure, and the condensate from inside the heating shaft can be recovered and returned to the boiler.

Cascade Dryers

Cascade or spouted dryers (Figure 4) are commonly used for drying grain, but they can be used for other types of biomass. Material is introduced to a flowing stream of hot air as it enters an enclosed chamber. The material is thrown into the air, then falls, or cascades, back to the bottom to be lifted again. Some of the material is drawn out through openings in the side of the chamber that control the residence time and amount of drying. *Superheated*

Steam Dryers

Most superheated steam dryers are similar to flash dryers, except that the fluid suspending the solids and providing heat is steam instead of air. Under normal operation, the wet material is mixed with enough superheated steam to dry the material and still end up with superheated steam. Typically 90% of the steam leaving the dryer is recirculated while 10% of the steam, representing the amount of water evaporated from the biomass, is removed and either condensed or used directly in other parts of the plant.

See also: Drying.

Biomass Energy

Biomass energy is energy generated or produced by living or once-living organisms. The most common biomass materials used for energy are plants, such as corn and soy, above. The energy from these organisms can be burned to create heat or converted into electricity.

Biomass contains energy first derived from the sun: Plants absorb the sun’s energy through photosynthesis, and convert carbon dioxide and water into nutrients (carbohydrates). The energy from these organisms can be transformed into usable energy through direct and indirect means. Biomass can be burned to create heat (direct), converted into electricity (direct), or processed into biofuel (indirect).

Thermal Conversion

Biomass can be burned by thermal conversion and used for energy. Thermal conversion involves heating the biomass feedstock in order to burn, dehydrate, or stabilize it. The most familiar biomass feedstocks for thermal conversion are raw materials such as municipal solid waste (MSW) and scraps from paper or lumber mills. Different types of energy are created through direct firing, co-firing, pyrolysis, gasification, and anaerobic decomposition.

Before biomass can be burned, however, it must be dried. This chemical process is called torrefaction. During torrefaction, biomass is heated to approximately 200 to 320°C (390 to 610°F). The biomass dries out so completely that it loses the ability to absorb moisture, or rot. It loses approximately 20% of its original mass, but retains 90% of its energy. The lost energy and mass can be used to fuel the torrefaction process.

During torrefaction, biomass becomes a dry, blackened material. It is then compressed into briquettes. Biomass briquettes are very hydrophobic, meaning they repel water. This makes it possible to store them in moist areas. The briquettes have high energy density and are easy to burn during direct or co-firing.

Direct Firing and Co-Firing

Most briquettes are burned directly. The steam produced during the firing process powers a turbine, which turns a generator and produces electricity. This electricity can be used for manufacturing or to heat buildings.

Biomass can also be co-fired, or burned with a fossil fuel. Biomass is most often co-fired in coal plants. Co-firing eliminates the need for new factories for processing biomass. Co-firing also eases the demand for coal. This reduces the amount of carbon dioxide and other greenhouse gases released by burning fossil fuels.

Pyrolysis

Pyrolysis is a related method of heating biomass. During pyrolysis, biomass is heated to 200 to 300°C (390 to 570°F) without the presence of oxygen. This keeps it from combusting and causes the biomass to be chemically altered.

Pyrolysis produces a dark liquid called pyrolysis oil, a synthetic gas called syngas, and a solid residue called biochar. All of these components can be used for energy. Pyrolysis oil, sometimes called bio-oil or biocrude, is a type of tar. It can be combusted to generate electricity and is also used as a component in other fuels and plastics as an alternative to crude oil.

Biochar is a type of charcoal. Biochar is a carbon-rich solid that is particularly useful in agriculture. Biochar enriches soil and prevents it from leaching pesticides and other nutrients into runoff. Biochar is also an excellent carbon sink. Carbon sinks are reservoirs for carbon-containing chemicals, including greenhouse gases.

Gasification

Biomass can also be directly converted to energy through gasification. During the gasification process, a biomass feedstock (usually MSW) is heated to more than 700°C (1,300°F) with a controlled amount of oxygen. The molecules break down, and produce syngas and slag.

Synthesis gas is a combination of hydrogen and carbon monoxide. During gasification, syngas is cleaned of sulfur, particulates, mercury, and other pollutants. The clean syngas can be combusted for heat or electricity, or processed into transportation biofuels, chemicals, and fertilizers. Synthesis gas can also be converted into fuel (such as synthetic natural gas). It can also be converted into methane and used as a replacement for natural gas.

Slag forms as a glassy, molten liquid and can be used to make shingles, cement, or asphalt.

Anaerobic Decomposition

Anaerobic decomposition is the process where microorganisms, usually bacteria, break down material in the absence of oxygen. Anaerobic decomposition is an important process in landfills, where biomass is crushed and compressed, creating an anaerobic (or oxygen-poor) environment.

In an anaerobic environment, biomass decays and produces methane, which is a valuable energy source. This methane can replace fossil fuels. In addition to landfills, anaerobic decomposition can also be implemented on ranches and livestock farms. Manure and other animal waste can be converted to sustainably meet the energy needs of the farm.

See also: Alternate Fuels.

Biomass Energy Systems

Biomass has to be produced either by the cultivation of dedicated crops (such as wood by means of short rotation forestry, perennial grasses), by harvesting forest and other residues (thinnings, straw, etc.), or by collecting biomass waste (such as sludge, organic industrial waste, and organic domestic waste). Next, the biomass has to be harvested or collected, then transported, and if necessary, it may have to be stored and transferred.

Biomass can be converted by means of numerous processes. The actual choice of a process will depend on the type and quantity of available biomass feedstock, the desired energy carrier(s) (end-use), environmental standards, economic conditions, and other factors.

Most biomass energy conversion processes can be divided into (i) thermochemical conversion and (ii) biochemical conversion routes, and (iii) mechanical processes. With respect to thermochemical conversion options, a distinction can be made between combustion, gasification and pyrolysis. Biochemical conversion options can be divided into digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (such as the production of ethanol). Extraction is another, mainly mechanical, process for producing an energy carrier from biomass (e.g., rapeseed oil from rapeseed). With regard to the energy carriers produced from biomass, a distinction can be made between the production of heat, electricity, and fuels.

See also: Bioconversion Platform, Thermoconversion Platform.

Biomass – Extraction

Extraction is a mechanical conversion process and two well-established technologies for oil extraction are (i) the simple screw press, which is a device for physically extracting the oil from the plant – this technology is well suited to small-scale production of oil as fuel or as foodstuff in rural areas, and (ii) solvent extraction, a chemical process which requires large, sophisticated equipment – this method is more efficient and extracts a greater percentage of the oil from the plant.

The process can be used to derive rapeseed oil from rapeseed. In this case, the process produces not only oil but also rapeseed cake, which is suitable for fodder. Approximately 3 tons of rapeseed is required per ton of oil.

Rapeseed oil can be esterified to obtain rapeseed methyl ester (RME) or biodiesel. This process is being used commercially on a substantial scale, especially in Europe.

See also: Biomass Extraction, Rapeseed.

Biomass Feedstocks

Consideration of biomass feedstocks for processes must go beyond such a simple representation as the van Krevelen diagram since the composition varies with the nature of the feedstock. For most agricultural residues, the heating values are even more uniform – approximately 6,450 to 7,300 Btu/lb, and the values for most woody materials are 7,750 to 8,200 Btu/lb. The moisture content is extremely important in determining the heating value of biomass as well as its suitability as a process feedstock. Air-dried biomass typically has approximately 15 to 20% moisture. The moisture content is also an important characteristic of coals, varying in the range of 2 to 30%. However, the bulk density (and hence energy density) of most biomass feedstocks is generally low, even after densification, approximately 10 and 40% of the bulk density of most fossil fuels. Liquid biofuels have comparable bulk densities to fossil fuels.

Most biomass materials are easier to gasify than coal because they are more reactive with higher ignition stability. This characteristic also makes them easier to process thermochemically into higher-value fuels such as methanol or hydrogen. Ash content is typically lower than for most coals, and sulfur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest.

Some biomass feedstocks stand out for their peculiar properties, such as high silicon or alkali metal contents – these may require special precautions for harvesting, processing, and combustion equipment. The mineral content can also vary as a function of soil type and the timing of feedstock harvest. In contrast to their fairly uniform physical properties, biomass fuels are rather heterogeneous with respect to their chemical elemental composition.

Among the liquid biomass fuels, biodiesel (vegetable oil ester) is noteworthy for its similarity to crude oil-derived diesel fuel, apart from its negligible sulfur and ash content. Bioethanol has only approximately 70% the heating value of crude oil distillates such as gasoline, but the sulfur content and the ash content are also low. Both of these liquid fuels have lower vapor pressure and flammability than their crude oil-based competitors – an advantage in some cases (e.g., use in confined spaces such as mines) but a disadvantage in others (e.g., engine starting at cold temperatures).

Plants offer a unique and diverse feedstock for chemicals. Plant biomass can be gasified to produce synthesis gas, a basic chemical feedstock and also a source of hydrogen for a future hydrogen economy. In addition, the specific components of plants such as carbohydrates, vegetable oils, plant fiber, and complex organic molecules known as primary and secondary metabolites can be utilized to produce a range of valuable monomers, chemical intermediates, pharmaceuticals, and materials:

Carbohydrates (starch, cellulose, sugars) are readily obtained from wheat and potato, while cellulose is obtained from wood pulp. The structures of these polysaccharides can be readily manipulated to produce a range of biodegradable polymers with properties similar to those of conventional plastics such as polystyrene foams and polyethylene film. In addition, these polysaccharides can be hydrolyzed, catalytically or enzymatically, to produce sugars, a valuable fermentation feedstock for the production of ethanol, citric acid, lactic acid, and dibasic acids such as succinic acid.

Vegetable oils are obtained from seed oil plants such as palm, sunflower, and soya. The predominant source of vegetable oils in many countries is rapeseed oil. Vegetable oils are a major feedstock for the oleo-chemicals industry (surfactants, dispersants, and personal care products) and are now successfully entering new markets such as diesel fuel, lubricants, polyurethane monomers, functional polymer additives, and solvents.

Plant fibers (lignocellulosic fibers) are extracted from plants such as hemp and flax can replace cotton and polyester fibers in textile materials and glass fibers in insulation products.

See also: Biofuels, Biomass.

Biomass – Fermentation

Fermentation is an anaerobic process that breaks down the glucose within organic materials, and the process is a series of chemical reactions that convert sugars to alcohol or acid. Yeast or bacteria are added to the biomass material, which feed on the sugars to produce ethanol and carbon dioxide. The process is used commercially on a large scale in various countries to produce ethanol from sugar crops (sugar cane, beet) and starch crops (maize, wheat).

The biomass is ground down, and the starch is converted by enzymes to sugars. Yeast then converts the sugars to ethanol. Pure ethanol is produced by distillation which is a relatively energy intensive step. Approximately 450 L of ethanol can be produced per tonne of dry corn. The remaining solids can be used as cattle feed. In the case of sugar cane, the remaining bagasse can also be used as fuel for boilers or gasification processes.

Conversion of lignocellulosic biomass (such as wood and grasses) requires acid or enzymatic hydrolysis before the resulting sugars can be fermented to ethanol. Such hydrolysis techniques are currently at the pre-pilot stage.

See also: Fermentation, Fermentation Chemistry.

Biomass Fuel

Solid biofuels such as wood or dried dung have been used since man learned to control fire. On the other hand, liquid biofuels for industrial applications was used since the early days of the car industry.

Nikolaus August Otto, the inventor of the combustion engine, conceived his invention to run on ethanol, while Rudolf Diesel, the inventor of the diesel engine, conceived it to run on peanut oil. Henry Ford originally had designed the Ford Model T, a car produced between 1903 and 1926, to run completely on ethanol, and the desire to mass produce electric cars did not come to fruition at that time. However, when crude oil began being cheaply extracted from deeper in the soil (thanks to oil reserves discovered in Pennsylvania and Texas), cars began using fuels from oil.

Nevertheless, before World War II, biofuels were seen as providing an alternative to imported oil in countries such as Germany, which sold a blend of gasoline with alcohol fermented from potatoes under the name Reichskraftsprit. In Britain, grain alcohol was blended with gasoline by the Distillers Company Ltd under the name Discol. After the World War II, cheap Middle Eastern oil lessened interest in biofuels. Then, with the oil shocks of 1973 and 1979, there was an increase in interests from governments and academics in biofuels. However, interest decreased with the counter-shock of 1986 that made oil prices cheaper again. However, the variation in the price of crude oil continues and is subject to political pressures from oil-producing countries.

The supply of crude oil, the basic feedstock for refineries and for the petrochemicals industry, is finite, and its dominant position will become unsustainable as supply/demand issues erode its economic advantage over other renewable feedstocks. This situation will be mitigated to some extent by the exploitation of more technically challenging fossil resources and the introduction of new technologies for fuels and chemicals production from natural gas and coal.

However, the use of fossil resources at current rates will have serious and irreversible consequences for the global climate. Consequently, there is a renewed interest in the utilization of plant-based matter as a raw material feedstock for the chemicals industry. Plants accumulate carbon from the atmosphere via photosynthesis, and the widespread utilization of these materials as basic inputs into the generation of power, fuels, and chemicals is a viable route to reduce greenhouse gas emissions.

Thus, the crude oil and petrochemicals industries are coming under increasing pressure not only to compete effectively with global competitors utilizing more advantaged hydrocarbon feedstocks but also to ensure that its processes and products comply with increasingly stringent environmental legislation.

The production of fuels and chemicals from renewable plant-based feedstocks utilizing state-of-the-art conversion technologies presents an opportunity to maintain competitive advantage and contribute to the attainment of national environmental targets. Bioprocessing routes have a number of compelling advantages over conventional petrochemicals production; however, it is only in the last decade that rapid progress in biotechnology has facilitated the commercialization of a number of plant-based chemical processes. It is widely recognized that further significant production of plant-based chemicals will only be economically viable in highly integrated and efficient production complexes producing a diverse range of chemical products. This biorefinery concept is analogous to conventional oil refineries and petrochemical complexes that have evolved over many years to maximize process synergies, energy integration, and feedstock utilization to drive down production costs.

See also: Biofuels, Biomass.

Biomass Fuel – Characteristics

Biomass can be converted to thermal energy, liquid, solid, or gaseous fuels, and other chemical products through a variety of conversion processes. These processes include physical conversion to *densified* fuels (e.g., pellets or cubes), thermal conversion through combustion or pyrolysis, chemical conversion, and microbial conversion or fermentation. The abundance of plant organic constituents and other physical and chemical characteristics vary significantly by plant type and the proportions of plant components such as leaves, stems, bark, and twigs in the feedstock.

The design of a biomass power or ethanol facility requires careful consideration of the effects that feedstock characteristics and composition have on the conversion process. Generating electricity and useful heat energy is most frequently done by direct combustion of biomass in a boiler. Energy content, moisture content, and chemical makeup are among the most important biomass characteristics affecting combustion processes. Biomass gasification yields a combustible gas that can be used to generate electricity. Particle size, energy content, moisture content, and volatiles are among the biomass characteristics affecting gasification.

The technology that is closest to commercialization for converting biomass to ethanol involves extracting complex carbohydrates, primarily cellulose and hemicellulose, from the biomass feedstock and reducing these components to simple sugars (a process called hydrolysis).

Cellulose is a long polymer of glucose, and it serves as a structural component of plant cell walls. It is often found in a composite mixture with hemicellulose and lignin. Hemicellulose is a polymer containing a variety of simple sugars and is more soluble than cellulose. Lignin is a ring-type carbohydrate that acts as cement in plant walls. The lignin portion of biomass is not converted to simple sugars through hydrolysis, but lignin can be burned to generate process heat and electricity.

Extracting the carbohydrates may involve “steam explosion” of the cell walls or dissolving the organic constituents with acids, enzymes, or organic solvents. Sugars resulting from hydrolysis are then converted into ethanol through microbial fermentation. The bulk and biochemical composition of the feedstock largely determine ethanol yield because these traits affect the hydrolysis and fermentation processes.

Biomass – Gasification

Although gasification is old technology with respect to coal-based feedstock, it is a developing technology with respect to biomass, since it was never fully embraced on a larger commercial scale. Biomass materials differ from conventional solids fuels such as coal based on the volatile matter. The volatile matter in the coal is less than 20%,

while it is up to 80% in biomass materials – the constituents of the gas are variable and are dependent upon the process parameters and the feedstock (Table B-20).

Table B-20 Composition of synthesis gas from biomass gasification.

Constituents	% v/v (dry, nitrogen free)
Carbon monoxide (CO)	28-36
Hydrogen (H ₂)	22-32
Carbon dioxide (CO ₂)	21-30
Methane (CH ₄)	8-11
Ethylene (C ₂ H ₄)	2-4

Gasification is the thermochemical conversion of biomass into gaseous fuels by means of partial oxidation of the biomass at high temperatures. The low calorific gas (low heat content gas) that is produced can be fired directly or be used for firing engines and gas turbine cycles and can also serve as syngas in the production of chemicals (e.g., methanol). Gasification is not a new technology; however, its use for the conversion of biomass into a viable fuel has only been investigated for the past thirty years. Production of synthesis gas, or syngas, from biomass can be accomplished by two broad categories of the chemical and thermal processes, namely catalytic routes and noncatalytic processes. Typically, noncatalytic processes require a high temperature of operation – as high as 1,300°C (2,370°F) – whereas catalytic processes can be operated at substantially lower temperatures. With advances in catalysis, the temperature requirement is expected to be reduced even further.

Two reactor types exist: (i) the fluidized bed reactor, which is used with large-scale gasification system, and (ii) the fixed bed reactor, which is employed for small-scale producer gas systems. There are three varieties of fixed bed reactor: (i) the updraft reactor, (ii) the downdraft reactor, and (iii) the crossdraft reactor. Each reactor type produces a different ratio of gases at different temperatures.

In the fluidized bed system, fluidizing gas and heat for the gasification can be supplied by the combustion of a hydrocarbon such as natural gas (methane) or propane in the absence of air. The particulates and char are removed using a high temperature cyclone.

The most common method of gasifying biomass is using an air-blown circulating fluidized bed gasifier with a catalytic reformer, even though there are many different variations. Most fluidized bed gasification processes use closed-coupled combustion with little or no intermediate gas cleaning. This type of process is typically operated at around 900°C (1,650°F), and the product gas from the gasifier contains hydrogen, carbon monoxide, carbon dioxide, water, methane, olefins, benzene, and tar. Gasification uses oxygen (or air) and steam to help the process conversion, just as coal gasification. While the effluent gas from the fluidized bed gasifier contains a decent amount of syngas compositions, the hydrocarbon contents are also quite substantial. Therefore, the gasifier effluent gas cannot be directly used as syngas for further processing for other liquid fuels or chemicals without major purification steps.

Indirect gasification is another gasification process technology that takes advantage of the unique properties associated with biomass. As such, indirect gasification of biomass is substantially different from most coal-based gasification process technologies. For example, biomass is low in sulfur, low in ash, highly reactive, and highly volatile. In an indirect gasification process, biomass is heated indirectly using an external means such as heated sands and a typical gaseous product from an indirect gasifier is close to a medium-Btu gas.

A promising concept is the biomass integrated gasification gasification/combined cycle (BIG/CC) system. Gas turbines can convert gaseous fuel to electricity with a high efficiency. An important advantage of BIG/CC systems is that the gas is cleaned before being combusted in the turbine which means that more compact and less costly gas cleaning equipment is required. The integration ensures high conversion efficiency; on a scale of 30-60 MW_e, net efficiencies of 40-50% (LHV basis of the incoming fuel) can be expected. BIG/CC systems offer a relatively high efficiency on a modest scale. This is important to limit transportation distances for the biomass delivered. A variety of biomass gasification processes are commercially applied.

Another process option for biomass gasification for syngas production involves the use of an entrained flow reactor. This type of process is operated at a high temperature, around 1,300°C (2,370°F), and without use of catalyst. The high temperature is necessary due to the fast reaction rate required for an entrained reactor whose reactor residence time is inherently short.

If a specific biomass feed has high ash content, which is not very typical for biomass, slag can be formed at such a high temperature. Learning from the research developments in coal gasification, a slagging entrained flow gasifier may be adopted for high-ash biomass conversion. Another important process requirement, in addition to high temperature and short residence time, is the particle size of solid feed that must be fine for efficient entrainment as well as for better conversion without mass transfer limit. However, pulverization or milling of biomass is energy-intensive and costly, in general. To facilitate an efficient size reduction of biomass feed, two options are most commonly adopted, viz., torrefaction and pyrolysis.

Production of synthesis gas from biomass by means of gasification also allows for the production of methanol or hydrogen, each of which may have a good future as transportation fuels. For the production of methanol or hydrogen, indirect or oxygen-blown gasification processes are favored because of the medium calorific gas that is produced by such processes.

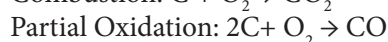
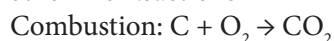
See Biomass – Pyrolysis, Gasification, Torrefaction.

Biomass – Gasification Principles

The biomass gasification is complex and proceeds primarily through a two-step process, pyrolysis followed by gasification. Pyrolysis is the decomposition of the biomass feedstock by heat. This step, also known as devolatilization, is endothermic and produces 75 to 90% volatile materials in the form of gaseous and liquid hydrocarbon derivatives. The remaining non-volatile material, containing high carbon content is referred to as char. Volatile hydrocarbon and char are subsequently converted to syngas in the second step, gasification.

While pyrolysis begins at temperature in excess of 500°C (930°F), gasification reactions are predominating at temperature nearing and excess of 1,000°C (1,830°F). The following are the details of the reactions during gasification process.

Exothermic Reactions



Endothermic Reactions



See also: Biomass – Gasification.

Biomass – Gasification Process

Biomass gasification is the complete conversion of biomass to gaseous products consisting of carbon monoxide (CO), hydrogen (H₂), and methane (CH₄), with traces of other gases depending on the character of the biomass feedstock.

This gaseous product is usually a low-to-medium Btu gas (producer gas) which can be used to run internal combustion engines (both compression and spark ignition), can be used as substitute for furnace oil in direct heat applications, and can be used to produce, in an economically viable way, methanol – an extremely attractive chemical which is useful both as fuel for heat engines as well as chemical feedstock for industry.

Since any biomass material can undergo gasification, this process is much more attractive than ethanol production or biogas where only selected biomass materials can produce the fuel.

The preliminary gasification of biomass in (preferably) pressurized circulating fluidized bed reactor with secondary processing of the obtained product gas in a slagging entrained flow gasifier is another option. Usually, little or no pretreatment of the biomass is needed (particle size up to 5 cm is acceptable) and that a wide range of biomass feedstock can be processed.

Similar to pyrolysis, the availability of some bed material in the product gas, which is fed into the entrained flow gasifier, is not a concern either, as it improves the properties of molten slag.

Maintaining the stability of the feed flow necessary for the safe operation of entrained flow gasifiers could be a problem, because circulating fluidized bed gasifiers are characterized by some variations in the product gas flow. In order to keep the amount of nitrogen in the product gas under control, the first step circulating fluidized bed gasification is performed with steam, not with air.

After being pyrolyzed in a low-temperature gasifier, biomass pyrolysis gas and char are fed to an entrained flow gasifier and a tar-free gas with high content of carbon monoxide and hydrogen is obtained. The clean gas is cooled down to approximately 200°C (390°F) in a heat exchanger, increasing thereby the overall energy efficiency of the process by producing high-quality steam for power and/or heat generation. Next, the gas is cleaned from dust particles (in a de-duster) and from components, other than carbon monoxide and hydrogen (in a washer). At the end, clean synthesis gas, consisting of carbon monoxide, is obtained. Sufficient gas cleaning represents a key point in syngas and liquids production.

The catalysts for the synthesis of liquid fuels and chemicals are easily poisoned even by small amounts of alkali metals, halides, sulfur compounds, and carbon dioxide which therefore have to be removed to ppm and even ppb levels.

Besides torrefaction, pyrolysis, and pre-gasification, there is a fourth option to convert biomass into a semi-finished material. This is the hydrothermal upgrading process (HTU process), which, under certain conditions, could be considered also as a pre-treatment alternative for biomass conversion.

See also: Biomass – Gasification, Carbo-V Process, Hydrothermal Upgrading Process, Torrefaction.

Biomass – Gasification Reactors

Biomass gasifiers can be classified in to three major groups which are (i) fixed bed reactors, comprising either updraft or downdraft mode, (ii) bubbling fluidized bed reactors, and (iii) circulating fluidized bed reactors.

The difference among each of the reactors is based on the means of supporting the biomass in the reactor vessel, the direction of flow of the biomass, the oxidant, and the way heat is supplied to the reactor. The fixed bed gasifiers are the oldest and simplest form of gasifiers. Although they are a simple, low-cost process, they are not suitable for large-scale production and limited to small-scale operations.

Large-scale biomass gasifiers employ one of two types of fluidized bed configurations: (i) the bubbling fluidized bed and (ii) the circulating fluidized bed or (iii) combination of both (indirectly fired) to maintain the bed temperature below the ash fusion temperature of the biomass ash.

Bubbling Fluidized Bed Gasifier

A bubbling fluidized bed consists of fine, inert particles of sand or alumina, which are selected based on their suitability of physical properties such as size, density, and thermal characteristics. The gas flow rate is chosen to maintain the bed in a fluidization condition, which enters at the bottom of the vessel. The dimension of the bed at some height above the distributor plate is increased to reduce the superficial gas velocity below the fluidization velocity to maintain the inventory of solids and to act as a disengaging zone. A cyclone is used to trap the smaller size particle that exit the fluidized bed, either return fines to the bed or to remove ash rich fines from the system.

Biomass is introduced either through a feed chute to the top of the bed or deep inside the bed. The deeper introduction of biomass into the bed of inert solids provides sufficient residence time for fines that would otherwise be entrained in the fluidizing gas. The biomass organics pyrolytically vaporize and are partially combusted in the

bed. The exothermic combustion provides the heat to maintain the bed temperature and to volatilize additional biomass.

The bed needs to be preheated to the startup temperature using hydrocarbon resources such as natural gas and fuel oil, either by direct firing or by indirect heating. After the bed reaches the biomass ignition temperature, biomass is slowly introduced into the bed to raise the bed temperature to the desired operating temperature which is normally in the range of 700 to 900°C (1,290 to 1,650°F). Bed temperature is governed by the desire to obtain complete devolatilization versus the need to maintain the bed temperature below the biomass ash fusion temperature. The advantages of the fluidized bed gasifiers are: (i) yield of a uniform product gas, (ii) able to accept a wide range of fuel particle sizes, including fines, (iii) exhibits a nearly uniform temperature distribution throughout the reactor, (iv) provides a high rate of heat transfer between inert material and biomass, aiding high conversion, with low tar. The disadvantage is formation of large bubbles at higher gas velocities, which bypass the bed reducing the high rate of heat/mass transfer significantly.

Circulating Fluidized Bed Gasifier

In a circulating fluid bed (CFB) the turbulent bed solids are collected, separated from the gas, and returned to the bed, forming a solids circulation loop. A circulating fluidized bed can be differentiated from a bubbling fluidized bed in that there is no distinct separation between the dense solids zone and the dilute solids zone. Lower bed density can be achieved with increase in gas flow rates in excess of transport velocity of the fluidized bed particles. The residence time of the solids in the circulating fluid bed is determined by the solids circulation rate, attrition of the solids, and the collection efficiency of the solids in the cyclones. The advantages of the circulating fluidized bed gasifiers are that they are (i) suitable for rapid reactions, (ii) high conversion rates possible with low tar and unconverted carbon, and (iii) high heat transport rates possible due to high heat capacity of bed material. The disadvantages are (i) temperature gradients occur in the direction of the solid flow, (ii) the size of fuel particles required to determine minimum transport velocity, (iii) high velocities may result in equipment erosion, and (iv) heat exchange less efficient than in the bubbling fluidized bed reactor.

Indirectly Heated Gasifier

The fluidizing media for the biomass gasification are either air and steam or pure oxygen and steam. Air-blown or directly heated gasifiers use the exothermic reaction between the oxygen and organics to provide the heat necessary to devolatilize biomass and to convert residual carbon rich chars. For directly heated gasifiers, the heat to drive the process is generated inside within the gasifier. When air is used, the product gas is diluted with nitrogen and typically has a dry basis calorific value of 110 to 160 Btu/ft³. The use of oxygen instead of air produces a medium heating value syngas, 265 to 400 Btu/ft³, suitable for combustion turbine application.

Oxygen production is expensive, and hence indirectly heated gasifiers which utilize twin bed concept similar to fluid catalytic crackers (FCC) that are being used in crude oil refining are being developed for generation of medium calorific syngas using air as fluidizing medium.

The syngas produced from the indirectly heated gasifiers is devoid of the nitrogen contamination, and hence they are also favored for other gas- to liquid-based technologies. The non-requirement of oxygen to generate medium heating value syngas, results in lower capital cost for the gasification plant.

If the gas turbines using fossil fuel (natural gas or diesel) which has heating value of approximately 885 Btu/ft³, needs to be interchangeable with the biomass syngas, higher heating values are preferred. In a natural-gas-fired turbine, the gas is only related to 2% v/v of the flow and the rest is air for dilution and combustion, while in contrast, syngas accounts for 14 to 16% v/v of the total gas.

The IGCC (Integrated Gasification Combined Cycle) uses air as the gasifying agent and requires modified turbine combustors to handle the low heating-value gas (110 to 190 Btu/ft³). The low calorific syngas up to 135 Btu/ft³ is only suitable for firing in the boiler or use in diesel engines.

Indirectly heated gasifiers in general generate syngas with a high percentage of hydrogen, methane, and C₂₊ compounds which directly contribute for the higher heating value of the syngas.

Similarly for the directly fired gasifiers, the higher range of hydrogen, methane, and C₂₊ components corresponds to the combustion using oxygen, leading to higher calorific value of the syngas. The absence of nitrogen (inert) in the

system largely helps to concentrate the composition of syngas with higher heating value components. Production of tars, chars, and volatile alkalis are problems associated with gasification which requires further cleaning before it is utilized in turbines for power generation.

The product stream at high pressure and temperature needs to be cleaned under hot conditions not lower than 540°C (1005°F) (tar dew point) in order to maximize the energy conversion efficiency. Thus, a hot cleanup system is required, for which either catalytic tar crackers or a thermal tar cracker could be utilized. A catalytic tar reformer will operate at temperatures comparable to gasifier temperature of 825°C (1,515°F), while a thermal cracker will typically operate at 870 to 980°C (1600 to 1,795°F). After the tar reformer/cracker, the product gas will be partially cooled to minimize the amount of alkali vapors, typically to 350 to 650°C. The product will then pass through a filter to remove solids. As gas turbine application limits the alkali to less than 25 ppb, much of alkali as well needs to be removed.

See also: Synthesis Gas Quality.

Biomass – Herbaceous

Herbaceous biomass is biomass from plants that have a nonwoody stem and which die back at the end of the growing season. This biomass includes most agricultural crops and grasses, including bamboo and wheat straw. Also, relatively young and essentially nonwoody parts of trees exhibit similar characteristics. In general, herbaceous biomass will have higher nutrient contents and lower lignin contents than wood. Herbaceous biomass is variable in composition depending on the time of year and on the type of tissue. Composition can also be strongly influenced by the availability of minerals or nutrients in the soil.

Herbaceous biomass is classified into cereal crops, pastures, oilseed crops, tubers and legumes, flowers, herbaceous biomass of gardens, parks, pruning, vineyards, orchards, and mixtures of all these. This biomass can be used raw (direct residues of the field) or processed (from the food industry).

Residues from cereal crops include the use of the following parts of the plant: dried stems, pods, and husks, as well as their mixtures. Of the grasslands are considered stems, shells, and their mixtures. In oil crops, stems, leaves, pods, rinds, and their mixtures are considered. The residues of the tuber crops are integrated by stems, leaves, roots, and mixtures of these. The stems, leaves, pods, and their mixtures can be harvested from legume crops, but it should be noted that the incorporation of legumes in an annual biomass cultivation system could reduce the nitrogen fertilizer requirements, which will reduce the inputs of bioenergy production. However, they also contribute to the anthropogenic emissions of nitrous oxide (NO₂) which, in this case, nitrous oxide comes mainly from the decomposition of legume residues.

Finally, from the cultivation of flowers, the waste from the plant (when the quality of these is not adequate), the stems, leaves, as well as their mixture can be used. For its part, processed residues can come from herbaceous residues without chemical treatment, as well as chemically treated herbaceous residues and its mixtures. This type of biomass is used mainly in combustion and co-combustion systems, where the technology is well developed, has high efficiency, and low emissions; nevertheless, herbaceous crops that have a high content of potassium which may be detrimental for biomass combustion equipment. It is also used, albeit to a lesser extent, in gasification systems in mixtures with other sources of biomass.

The most abundant form of herbaceous biomass in the world, particularly in European countries, is straw, which is obtained during the annual production of cereals in a proportion of 0.6 to 0.8 tons of straw per ton of grain in the field. In countries where crop productivity is high (in the order of 8 to 10 tons of grain per hectare), the amount of straw per hectare can be between 6 and 8 tons and much of it has been removed for the next crop cycle.

Herbaceous biomass contains variable amounts of cellulose, hemicellulose, and lignin, and a small amount of other extractive, usually perennial, with looser fibers. The relative proportions of cellulose and lignin is one of the determining factors to identify the suitability of plant species for further processing as energy crops (Table B-21).

Table B-21 Approximate composition of herbaceous biomass gas from different sources.

Properties	Herbaceous biomass type	
	Wheat straw	Barley straw
Moisture (% w/w)	16	30
Volatile material (% w/w)	59	46
Fixed carbon (% w/w)	21	18
Ash (% w/w)	4	6
Net calorific value (MJ/kg)	18.6	16.1
C (% w/w)	48.5	45.7
H (% w/w)	5.5	6.1
O (% w/w)	3.9	38.3
N (% w/w)	0.3	0.4
S (% w/w)	0.1	0.1

Switchgrass, a type of fine-stemmed herbaceous biomass, has been used in the United States as a herbaceous cultivation model, has a calorific value comparable to that of wood, but with a lower moisture content; it also has a low content of ash and alkalis, indicating that it could be an adequate fuel for combustion. The main difficulty of this type of biomass is the production of slag at the time of gasification, associated with the ash content. To avoid slag production, the temperature can be reduced, but this results in the loss of carbon. The gas formed in the gasifier contains impurities such as particles, tar, nitrogen compounds, sulfur compounds, and alkaline compounds.

See also: Biomass.

Biomass – Land Requirements

If biomass is to play a major role in the energy supply of the world, energy farming is required. However, it is uncertain whether fallow land will be available to produce biomass for energy instead of food. The main stimulus in the European Union and the United States for introducing non-food crops in agriculture is the surplus production of food. Worldwide food demand is expected to increase considerably, but the amount and type of food that will be required depend on many factors. Population growth, as well as increasing incomes, may result in shifts to more protein-rich diets; both lead to increased demand for food crops. Loss of agricultural land caused by erosion, limited water resources and the increased demand for land for urbanization, infrastructure, and also preservation of nature all limit the possibilities for energy crops.

The availability of land for energy farming, however, does not depend only on the availability of agricultural land. Degraded land, for instance, which is not really suitable for food crops can represent a large potential for energy farming. At the same time, energy crops may help restore these damaged soils. Yields, however, will generally be lower than from good quality land.

Land that is needed to grow energy crops competes with land used for food and wood production unless surplus land is available. Furthermore, the demand for biomass (especially woody biomass) as a renewable energy source has increased continuously in recent years, especially for the direct provision of heat and power generation. However, the biomass potential is limited due to technical constraints and ecological restrictions, as well as the sustainability principles of land management, leading to a predicted supply shortfall.

To avoid competition with food and feed production land, there is the need to establish marginal sites with low soil quality, but sufficient water availability. Tree species capable of stump sprouting, such as poplar, willow, and black locust, can attain high biomass increments on cropland with low soil quality, but sufficient water supply due to their low nutrient requirements and deep-reaching roots. For example, sites for biomass production can be established on cropland with a low depth-to-groundwater table that poplars or willows with deep-reaching roots can utilize, but is inaccessible to annual cultures. The annual crop yield is typically low on croplands with low soil quality. Therefore,

these lands can be seen as agricultural marginal sites, where the combination of yields and prices barely covers the cost of production.

There is the need to conduct an assessment of the potential for land use based on (i) hydrological and climatic conditions, (ii) restrictions by various boundaries, from the technical, ethical, and ecological standpoints, and (iii) energy potential, considering the effect of global climate change.

See also: Biomass.

Biomass – Liquefaction

Biomass liquefaction is the conversion of solid (cellulosic) biomass materials to oil. During the mid-to-late 1980s, commercial interest of the thermochemical conversion of biomass focused on liquefaction. Unlike the initial gasification studies, the preliminary liquefaction studies utilized woody biomass, or lignocellulose material, as the feedstock. Woody biomass was considered superior to that of corn stover due to its potentially lower cost and greater availability.

Pyrolysis is the process of heating biomass in the lack of oxygen or in the presence of a limited amount of oxygen. The pyrolysis oil can be used directly as a fuel or as an intermediate for production of chemicals.

Fast pyrolysis is a thermal decomposition process operating at moderate temperatures (450 to 600°C, 840 to 1,110°F), with high heat transfer rates to the biomass particles and a short residence time. Under these conditions, organic vapors, gases, and char are produced. A short residence time is required to obtain the maximum yield of the liquid.

The vapors are condensed to produce pyrolysis oil (often referred to as bio-oil). Yields of liquid products as high as 79% of the initial dry weight of the biomass can be achieved. Generally, the process produces little or no waste and either the pyrolysis gas or charcoal is used to heat the reactor and the other can be used to supplement the other in heating, dry the feedstock, the charcoal can be sold as a byproduct, or the pyrolysis gas can be used to fuel a gas engine.

Pyrolysis oil is greenhouse gas neutral, does not produce SO_x (sulfur dioxide) emissions and produces approximately half of the NO_x (nitrogen oxide) emissions compared to fossil fuels.

See also: Biofuels, Biomass, Biomass – Liquefaction, Biomass To Liquids, Torrefaction.

Biomass Power

Biomass power is carbon-neutral electricity generated from renewable organic waste that would otherwise be dumped in landfills, openly burned, or left as fodder for forest fires. When burned, the energy in biomass is released as heat.

See also: Biomass Energy, Biomass to Energy.

Biomass – Power Facility

Feedstock requirements for a biomass power facility are dependent upon the capacity of the facility and, to a lesser extent, the efficiency of a specific technology. Dramatic reductions in demand, on a normalized basis, are achievable with increased size of the facility. A 5-MW direct combustion (stoker) power plant has a much higher heat rate than a larger facility. Indeed the larger plant may be approximately 50% more efficient than the smaller installation. The major reason for the higher efficiencies at larger sizes is the increased temperature and pressure that can be economically accommodated in the big facilities to supply larger turbines.

Fuel characteristics greatly affect the combustion process and therefore the decision process for choosing combustion technologies. The most common problems associated with the direct combustion of wood are boiler slagging and fouling, erosion and corrosion, combustion instability, and particulate carryover.

Fuel characteristics that should be analyzed include heating value, moisture content, ash content, sodium and potassium quantities, particle size distribution, ash fusion temperature, and sulfur content. Physical fuel characteristics such as density and particle size affect combustion as well as material handling considerations. Changes in fuel density could cause combustion to occur in the wrong place in the boiler, upsetting the heat transfer scheme and therefore the boiler efficiency.

Biomass Properties

The properties of biomass that have a significant bearing on its thermal conversion are its relatively high moisture, oxygen, hydrogen, and volatile matter content, and low heating value. The high oxygen and hydrogen contents account for the high proportion of volatile matter and consequent high yields of gases and liquids on pyrolysis. A relatively high water yield results from the high oxygen concentration in biomass, and which consumes considerable hydrogen. Consequently, the advantages of the high H/C ratio associated with biomass are not reflected in the products to the extent that might be expected. In fact, pyrolysis gases can be deficient in pure hydrogen and pyrolysis liquids are highly oxygenated, viscous tars.

An additional and significant source of water vapor in biomass gases is the high moisture content of the source materials. In countercurrent flow schemes such as the Lurgi moving bed gasifier, this water is evolved in the relatively low temperature drying and pyrolysis zones and does not partake in gas phase or carbon-steam gasification reactions.

On the other hand, in fluidized bed systems, the moisture is evolved in the high- temperature well-mixed reaction zone and therefore does participate in the reactions. If the system is directly heated and air-blown, the additional heat required to evaporate the water will result in more nitrogen being introduced, and more carbon dioxide being produced, so reducing the calorific value of the product gas. As the gas from air-blown processes is, in any case, a low-calorific value product, this factor is probably of little consequence other than with very wet feedstock. In oxygen-blown systems, however, the additional pure oxygen required and higher carbon dioxide content of the medium calorific value off-gas may be of sufficient impact to dictate some degree of drying as a pretreatment.

Apart from drying, additional beneficiation may be undertaken to yield a resource of higher energy density. These operations will normally be undertaken at the source, so transport and subsequent storage costs may be reduced as well. Beneficiation steps include size reduction and densification. Waste heat, if available, may be used for drying, while size reduction and compression to form pellets or briquettes is estimated to require less than 2% of the energy in the dry biomass. Nevertheless, these operations are time consuming, and can be either labor or capital intensive.

Some advantages of biomass over conventional fossil fuels are the low sulfur content and highly reactive char. In addition, biomass materials do not cake and can therefore be easily handled in both fluidized and moving bed reactors. Finally, catalyst poisons are not present in biomass in significant concentrations. This can be important for the initial thermal processing as well as for subsequent upgrading operations.

Biomass – Pyrolysis

Biomass can be converted into gas, liquid, and char via pyrolysis (Table B-22). The exact proportion of the end products is dependent on the pyrolysis process parameter, such as the feedstock, the temperature, the pressure, and the residence time in the reaction zone). Thus, in fact, pyrolysis of biomass is an important process option, either as a pretreatment for gasification or as an independent process treatment. Pyrolysis takes place actively at a temperature on the order of 500°C (930°F) and produces gases and a liquid product (bio-oil). In fact, the pyrolysis of biomass is quite similar, as a process treatment, to oil shale pyrolysis and coal pyrolysis.

Table B-22 A general flow scheme for biomass conversion by pyrolysis.

Feedstock	Process	Products (primary)	Products (secondary)
Biomass →	550°C/no oxygen	Char	Heat
			Power generation
	Condensation	Vapors	Hydrogen
			Chemicals
		Liquids	Fuels
			Chemicals

Bio-oil production via biomass pyrolysis is typically carried out via flash pyrolysis. The produced oil can be mixed with char to produce a bio-slurry, which can be more easily fed to the gasifier for efficient conversion. The slurry is pumpable and alleviates technical difficulties involved in solid biomass handling.

Typical end products are pyrolysis oil, char, and gas. The oil and char are more economical to transport than the original biomass feedstock and have heating values on the order of 10,000 Btu/lb and 12,000 Btu/lb, respectively. The pyrolysis gas, which has a nominal heating value of 150 Btu/scf, is not considered an end product since it is directly used in the cogeneration system.

The conversion of biomass to crude oil can have an efficiency of up to 70% for flash pyrolysis processes. The bio-oil (biocrude) can be used in engines and turbines and has the potential to be used as a refinery feedstock, although issues need to be overcome. These include poor thermal stability and corrosivity of the oil. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications.

See also: Biofuels, Biomass, Biomass – Liquefaction, Torrefaction.

Biomass – Synthesis Gas Production

Gasification is the process of gaseous fuel production by partial oxidation of a solid fuel. This means in common terms to burn with oxygen deficit. The gasification of coal is well known, and has a history back to year 1800. The oil-shortage of World War II imposed an introduction of almost a million gasifiers to fuel cars, trucks, and busses. One major advantage with gasification is the wide range of biomass resources available, ranging from agricultural crops, and dedicated energy crops to residues and organic wastes. The feedstock might have a highly various quality, but still the produced gas is quite standardized and produces a homogeneous product. This makes it possible to choose the feedstock that is the most available and economic at all times.

Gasification occurs in a number of sequential steps: (i) drying to evaporate moisture, (ii) pyrolysis to give gas, vaporized tars or oils and a solid char residue, and (iii) gasification or partial oxidation of the solid char, pyrolysis tars and pyrolysis gases.

Not all the liquids from the pyrolysis are converted to syngas, due to physical limitations of the reactor and chemical limitations of the reactions. These residues form contaminant tars in the product gas, and have to be removed prior to a Fischer-Tropsch reactor. Other impurities in the producer gas are the organic BTX [benzene, toluene and xylene (benzene components with one or two methyl groups attached)], and inorganic impurities as NH_3 , HCN , H_2S , COS and HCl . There are also volatile metals, dust, and soot. The tars have to be cracked or removed first, to enable the use of conventional dry gas cleaning or advanced wet gas cleaning of the remaining impurities. There are mainly three ways of tar removing/cracking: thermal cracking, catalytic cracking, or scrubbing.

Despite the long experience with gasification of biomass, there are some problems with large-scale reliable operation. No manufacturer of gasifier is willing to give full guarantee for the technical performance of their gasification technology. Though they are sold commercially, they are not delivered with the same kind of operational guarantee as e.g., a gas turbine. This shows the limited operational experience and lack of confidence in the technology, but in comparison with alternative routes to utilize cellulosic biomass gasification is well proven and one of the possible technologies to be introduced commercially as a major part of the energy route to biofuel.

The production of high-quality syngas from biomass, which is later used as a feedstock for biomass-to-liquids production, requires particular attention. This is due to the fact that the production of synthesis gas from biomass is indeed the novel component in the gas-to-liquids concept – obtaining syngas from fossil raw materials (natural gas and coal) is a relatively mature technology.

Various gasification concepts have been developed over the years, mainly for the purposes of power generation. However, efficient biomass-to-liquids production imposes completely different requirements for the composition of the gas because for power generation, the gas is used as a fuel, while in biomass-to-liquids processing, it is used as a chemical feedstock to obtain other products. This difference has implications with respect to the purity and composition of the gas.

The calorific value of the gas is the prime factor for power generation – the higher the value, the better. Hence, the availability in the gas of any compounds that increase calorific value is generally welcomed – product gas, which contains carbon monoxide (CO), hydrogen (H_2) and various hydrocarbon derivatives [methane (CH_4), ethylene ($CH_2=CH_2$), ethane (C_2H_6), tar, and char]. The presence of inert components [water (H_2O), carbon dioxide (CO_2), and nitrogen (N_2)] is also acceptable, provided it is kept within certain limits. In contrast, for biomass-to-liquids production, the amount of carbon monoxide and hydrogen is important. The presence of other hydrocarbon derivatives and inert components should be avoided or at least kept as low as possible.

The amount of components (primarily hydrocarbon derivatives) other than carbon monoxide and hydrogen can be reduced via their further transformation into carbon monoxide and hydrogen. This is, however, rather energy intensive and costly (two processes – gasification and transformation). As a result, the overall energy efficiency of syngas production and of biomass-to-liquids processing is also reduced.

The amount of various components can be minimized via a more complete decomposition of biomass, thereby preventing the formation of undesirable components at the gasification step. This approach seems to be more appropriate for energy efficiency. The minimization of the content of various hydrocarbon derivatives is achieved by increasing temperatures in the gasifier, along with shortening the residence time of feedstocks inside the reactor. Because of this short residence time, the particle size of feedstocks should be small enough (in any case – smaller than in gasification for power generation) in order that complete and efficient gasification can occur.

In gasification for power generation, typically, air is employed as an oxidizing agent, as it is indeed the cheapest among all possible oxidizing agents. However, the application of air results in large amounts of nitrogen in the product gas, since nitrogen is the main constituent of air. The presence of such large quantities of nitrogen in the product gas does not hamper (very much) power generation, but it does hamper liquids production. Removing this nitrogen via liquefaction under cryogenic temperatures is extremely energy intensive, reduces substantially the overall biomass-to-liquids energy efficiency, and increases costs. Among other potential options (steam, carbon dioxide, carbon monoxide), from a techno-economic point of view, oxygen appears to be the most suitable oxidizing agent for biomass-to-liquids manufacturing.

The air-blown direct gasifiers operated at atmospheric pressure and used in power generation – fixed bed updraft and downdraft and fluidized bed bubbling and circulating – are not suitable for biomass-to-liquids production. In addition, downdraft fixed bed gasifiers face severe constraints in scaling and are fuel inflexible, being able to process only fuels with well-defined properties.

Updraft fixed bed gasifiers have fewer restrictions in scaling (usually up to 10 MW), but the produced gas contains a lot of tars and methane. However, fluidized bed gasifiers generally do not encounter limitations in scaling and are more flexible concerning the particle size of fuels. Nevertheless, they still have limited fuel flexibility, due to a risk of slagging and fouling, agglomeration of bed material, and corrosion. The operating temperatures of air-blown fluidized bed gasifiers are therefore kept relatively low (800 to 1,000°C, 1,470 to 1,830°F), which implies incomplete decomposition of feedstocks, unless long residence times are used.

Fluidized bed gasifiers (especially the bubbling bed gasifiers) tend to contaminate the product gas with dust. The oxygen-blown atmospheric or pressurized circulating fluidized bed gasifiers and the steam-blown gas or char indirect gasifiers are better solutions for biomass-to-liquids processes. Both gasifying concepts significantly reduce the amount of nitrogen in the product gas. In the first case, it is achieved via substituting air with oxygen. In the second case, nitrogen ends up in the flue gas, but not in the product gas, because gasification and combustion are separated – the energy for the gasification is obtained by burning the chars from the first gasifier in a second reactor.

Nonetheless, both oxygen-blown circulating bed gasifiers and steam-blown indirect gasifiers still present some major weak points with regard to biomass-to-liquids processes. In the former case, the issues related to the necessity for further cracking of the unconverted hydrocarbon derivatives and with the high dust emissions are still relevant. In the latter case, these two drawbacks can be overcome, but at the expense of a significant increase in capital costs, since two reactors are needed instead of just one. In fact, the case of the gas indirect gasifier also involves a second reactor. Finally, indirect gasifiers carry a higher risk of malfunctioning and are less reliable, because of their more sophisticated configuration.

Considering the above reasons, the pressurized oxygen-blown direct entrained flow gasifier appears to be the most suitable gasification concept to obtain synthesis gas for later biomass-to-liquids processes. Entrained flow gasifiers do not encounter severe scaling restrictions, and their capacity can easily be of several hundred MW. They also represent a mature technology for coal (not for biomass!), which has been employed for years. Entrained flow gasifiers operate at elevated pressures and much higher temperatures (1,200 to 1,500°C, 2,190 to 2,730°F) than other gasifiers (usually below 900°C, 1,650°F). The residence time of the fuel is also much shorter (a few seconds) compared to that in other gasifiers.

For a complete transformation of the feedstock into synthesis gas within such short residence time, its particle size also has to be smaller than that required for other gasifiers – not larger than 1 mm, typically below 0.1 mm (100 µm, 100 microns). With such extreme conditions, almost tar-free synthesis gas with high content of carbon monoxide and hydrogen is obtained. This high conversion rate is also facilitated by the high reactivity and volatility of biomass. Conversely, the maximization of the liquids yield, i.e., of the content of CO and H₂ in the product gas, results in 10 to 15% lower total transformation efficiency (when other useful products from gasification are also counted) compared to other gasifying concepts.

Many feedstocks have high content of ash, which under high temperature turns into molten slag. Molten slag also retains some undesirable compounds of biomass, e.g., heavy metals. The removal of molten slag from the bottom of the reactor has to be incorporated into its design – a slagging-type entrained flow gasifier. In order to improve slag properties, the addition of fluxing material (silica sand or limestone) is necessary. In contrast, in non-slugging entrained flow gasifiers, the removal of molten slag is not foreseen. Hence, non-slugging gasifiers are fuel inflexible, suitable only for clean feedstocks with low mineral (ash) content (less than 1%), e.g., oils.

The energy efficiency of gasification is further reduced by the removal of large quantities of inert gas (usually carbon monoxide) from the product gas. Inert gas is employed as a medium for lock hopper pressurization and pneumatic feeding of pulverized material (a mandatory feeding option for finely pulverized fuels) into the reactor. The amount of inert gas depends on the bulk density of fuels – the lower the density, the larger the amount. The low bulk density of biomass implies large consumption of carbon dioxide, and alternative forms of biomass feedstock (via pre-treatment) have to be considered for entrained flow gasifiers. The most feasible biomass pre-treatment options are torrefaction, pyrolysis, and pre-gasification.

See also: Biomass – Gasification, Gasifiers, Synthesis Gas.

Biomass to Energy

The old way of converting biomass to energy, practiced for thousands of years, is simply to burn it to produce heat (one of final forms of energy). The problems with burning biomass are that much of the energy is wasted and that it can cause some pollution if it is not carefully controlled. A number of non-combustion methods are available for converting biomass to energy. These processes convert raw biomass into a variety of gaseous, liquid, or solid fuels that can then be used directly in a power plant for energy generation. The carbohydrates in biomass, which are comprised of oxygen, carbon, and hydrogen, can be broken down into a variety of chemicals, some of which are useful

fuels. This conversion can be done in three ways: (i) thermochemical methods, (ii) biochemical methods, and (iii) physical methods.

When plant matter is thermally decomposed, it breaks down into various gases, liquids, and solids. These products can then be further processed and refined into useful fuels such as methane and alcohol. Biomass gasifiers capture methane released from the plants and burn it in a gas turbine to produce electricity. Another approach is to take these fuels and run them through fuel cells, converting the hydrogen-rich fuels into electricity and water, with few or no emissions.

Biochemical methods of biomass breakdown involve the use of bacteria, yeasts, and enzymes, which also break down carbohydrates. Fermentation, the process used to make wine, changes biomass liquids into alcohol, a combustible fuel. A similar process is used to turn corn into grain alcohol or ethanol, which is mixed with gasoline to make gasohol. Also, when bacteria break down biomass, methane and carbon dioxide are produced. This methane can be captured, in sewage treatment plants and landfills, for example, and burned for heat and power.

Biomass oils, like soybean and canola oil, can be chemically converted into a liquid fuel similar to diesel fuel, and into gasoline additives. Cooking oil from restaurants, for example, has been used as a source to make biodiesel for trucks.

See also: Biofuels, Biochemical Platform, Biomass Conversion, Thermochemical Platform.

Biomass to Liquids

The biomass-to-liquid (BTL) process concept is a process for converting various types of biomass to liquid fuels and uses a variety of processes (Table B-23).

Table B-23 Conversion of biomass to fuels.

Starch/sugar crops		
Hydrolysis		
Sugar		
Fermentation		
Refining		
Ethanol		
Lignocellulose biomass		
Pyrolysis/liquefaction	Gasification	Anaerobic digestion
Bio-oil	Synthesis Gas	Bio-oil
Hydrotreating	Fischer-Tropsch	Biogas
Hydrocarbon fuels	Hydrocarbon fuels	Gas treating
		Methane
Oil-producing plants		
Pretreatment		
Vegetable oil		
Esterification		
Biodiesel		

There are two types of biomass feedstock that can be employed to produce BTL fuels – woody and herbaceous. Woody feedstock comprises wood chips, wood powder and sawdust, obtained from ordinary forestry (wood logs), short-rotation forestry, various wood residues, and wood waste. Herbaceous feedstock includes chaffed dedicated energy crops and straw.

Owing to biomass composition, woody feedstock is better suited for energy applications than herbaceous feedstock. Woody biomass also has a larger production potential for energy (including BTL) application; however, the production potential of herbaceous biomass is currently under-explored as the path to useful products is open, for example (Table B-24):

Table B-24 Routes to liquid fuels from biomass.

Biomass						
	Pretreatment					
		Gasification				
			Synthesis gas			
			Fischer-Tropsch			
				Upgrading		
					Gasoline	
					Diesel fuel	
			Methanol synthesis			
				Methanol-to-gasoline		
						LPG
						Gasoline

Biomass pyrolysis is a process by which a biomass feedstock is thermally degraded in the absence of air/oxygen. It is used for the production of solid (charcoal), liquid (tar and other organics), and gaseous products. These products are of interest as they are possible renewable sources of energy. The study of pyrolysis is gaining increasing importance, as it is not only an independent process but it is also a first step in the gasification or combustion process, and has many advantages over other renewable and conventional energy sources. The actual reaction scheme of pyrolysis of biomass is extremely complex because of the formation of over a hundred intermediate products.

Plasma pyrolysis provides high temperature and high energy for reaction as the reaction sample is rapidly heated up to a high temperature. This review also covers the experimental and modeling study status of plasma-assisted pyrolysis.

Biofuels produced via gasification routes include direct gasoline and diesel substitutes made from gas-to-liquid processes (i.e., the Fischer-Tropsch process), methanol, ethanol, mixed alcohols, and hydrogen. Gas-to-liquids technologies are utilized commercially using natural gas or stranded natural gas as feedstock. Coal was used extensively by Germany in WWII and is still used in the Sasol (South Africa) facilities for gasoline and diesel fuel synthesis along with a wide variety of other products.

In a biomass-to-liquids process, the feedstock undergoes a pretreatment or selection (sizing, drying, and sorting) and is then gasified in a reactor. The gas product (carbon monoxide, hydrogen, low-boiling hydrocarbon derivatives, tars, and particulate material) undergoes extensive cleanup to remove catalyst poisons and other undesirable components. This is followed by gas processing/reforming where the hydrogen/carbon monoxide ratio is adjusted before entering the (Fischer-Tropsch) synthesis reactor. The liquid synthesis reactor contains catalyst material and operates at elevated pressure and temperature forming hydrocarbon compounds or alcohols from the synthesis gas. The liquids can be further refined to the desired end product.

See also: Biomass – Gasification, Biomass to Syngas, Synthesis Gas.

Biomass Waste

Biomass is the material derived from plants that use sunlight to grow which include plant and animal material such as wood from forests, material left over from agricultural and forestry processes, and organic industrial, human, and animal wastes. Biomass comes from a variety of sources which include (alphabetically and not by preference or use):

- Agricultural residues such as straw, stover, cane trash and green agricultural wastes
- Agro-industrial wastes, such as sugarcane bagasse and rice husk
- Animal wastes
- Food processing wastes
- Forestry plantations
- Forestry residues
- Municipal solid wastes (MSW)
- Industrial wastes, such as black liquor from paper manufacturing
- Sewage
- Wood from natural forests and woodlands

The energy contained in biomass originally came from the sun. Through photosynthesis, carbon dioxide in the air is transformed into other carbon-containing molecules (e.g., sugars, starches, and cellulose) in plants. The chemical energy that is stored in plants and animals (animals eat plants or other animals) or in their waste is called bio-energy.

When biomass is burned, it releases its energy, generally in the form of heat. The biomass carbon reacts with oxygen in the air to form carbon dioxide. If fully combusted, the amount of carbon dioxide produced is equal to the amount which was absorbed from the air while the plant was growing.

In nature, if biomass is left lying around on the ground, it will break down over a long period of time, releasing carbon dioxide and its store of energy slowly. By burning biomass, its store of energy is released quickly and often in a useful way. So converting biomass into useful energy imitates the natural processes but at a faster rate.

Biomass wastes can be transformed into clean energy and/or fuels by a variety of technologies, ranging from conventional combustion process to state-of-the-art thermal depolymerization technology. Besides recovery of substantial energy, these technologies can lead to a substantial reduction in the overall waste quantities requiring final disposal, which can be better managed for safe disposal in a controlled manner while meeting the pollution control standards.

Biomass waste-to-energy conversion reduces greenhouse gas emissions in two ways. Heat and electrical energy are generated which reduces the dependence on power plants based on fossil fuels. The greenhouse gas emissions are significantly reduced by preventing methane emissions from landfills. Moreover, waste-to-energy plants are highly efficient in harnessing the untapped sources of energy from wastes.

Biomass energy projects provide major business opportunities, environmental benefits, and rural development. Feedstocks can be obtained from a wide array of sources without jeopardizing the food and feed supply, forests, and biodiversity in the world and include (i) agricultural residues, (ii) animal waste, (iii) forestry residue, (iv) wood waste, (v) industrial waste, (vi) municipal solid waste, and (vii) sewage.

Agricultural residues encompasses all agricultural wastes such as bagasse, straw, stem, stalk, leaves, husk, shell, peel, pulp, stubble, etc. Large quantities of crop residues are produced annually worldwide, and are vastly underutilized. Rice produces both straw and rice husks at the processing plant which can be conveniently and easily converted into energy. Significant quantities of biomass remain in the fields in the form of cob when maize is harvested which can be converted into energy. Sugar cane harvesting leads to harvest residues in the fields, while processing produces fibrous bagasse, both of which are good sources of energy. Harvesting and processing of coconuts produces quantities of shell and fiber that can be utilized. The current farming practice is usually to plough these residues back into the soil, or they are burnt, left to decompose, or grazed by cattle. These residues could be processed into liquid fuels or thermochemically processed to produce electricity and heat. Agricultural residues are characterized by seasonal availability and have characteristics that differ from other solid fuels such as wood, charcoal, and char briquette. The main differences are the high content of volatile matter and lower density and burning time.

Animal waste represents a wide range of biomass that can be used as sources of biomass energy. The most common sources are animal and poultry manures. In the past, this waste was recovered and sold as a fertilizer or simply spread onto agricultural land, but the introduction of tighter environmental controls on odor and water pollution means that some form of waste management is now required, which provides further incentives for waste-to-energy conversion. The most attractive method of converting these waste materials to useful form is anaerobic digestion which gives biogas that can be used as a fuel for internal combustion engines, to generate electricity from small gas turbines, burnt directly for cooking, or for space and water heating.

Forestry residues are generated by operations such as thinning of plantations, clearing for logging roads, extracting stem-wood for pulp and timber, and natural attrition. Harvesting may occur as thinning in young stands, or cutting in older stands for timber or pulp that also yields tops and branches usable for biomass energy. Harvesting operations usually remove only 25 to 50% of the volume, leaving the residues available as biomass for energy. Stands damaged by insects, disease, or fire are additional sources of biomass. Forest residues normally have low density and fuel values that keep transport costs high, and so it is economical to reduce the biomass density in the forest itself.

Wood wastes generated by the wood processing industries primarily include sawmilling, plywood, wood panel, furniture, building component, flooring, particle board, molding, jointing, and craft industries. Wood wastes generally are concentrated at the processing factories, e.g., plywood mills and sawmills. The amount of waste generated from wood processing industries varies from one type of industry to another depending on the form of raw material and finished product. Typically, the waste from wood industries such as saw millings and plywood, veneer, and others are sawdust, off-cuts, trims, and shavings. Sawdust arises from cutting, sizing, re-sawing, and edging, while trims and shaving are the consequence of trimming and smoothing of wood. In general, processing of wood in the furniture industries will lead to waste generation of almost half (45 %) of wood. Similarly, when processing wood in a sawmill, the waste will amount to more than half (52 %) of the wood.

Industrial wastes are generated by the food industry which produces a large number of residues and by-products that can be used as biomass energy sources. These waste materials are generated from all sectors of the food industry with everything from meat production to confectionery producing waste that can be utilized as an energy source. Solid wastes include peelings and scraps from fruit and vegetables, food that does not meet quality control standards, pulp and fiber from sugar and starch extraction, filter sludge, and coffee grounds. These wastes are usually disposed of in landfill dumps.

Liquid wastes are generated by washing meat, fruit and vegetables, blanching fruit and vegetables, pre-cooking meats, poultry and fish, cleaning and processing operations, as well as wine making. These wastewaters contain sugars, starches, and other dissolved and solid organic matter. The potential exists for these industrial wastes to be anaerobically digested to produce biogas, or fermented to produce ethanol, and several commercial examples of waste-to-energy conversion already exist. The pulp and paper industry is considered to be one of the highly polluting industries and consumes a large amount of energy and water in various unit operations. The wastewater discharged by this industry is highly heterogeneous as it contains compounds from wood or other raw materials, processed chemicals, as well as compound formed during processing. Black liquor can be judiciously utilized for production of biogas using anaerobic digestion technology.

Municipal solid wastes are produced and collected each year with the vast majority being disposed of in open fields. The biomass resource in municipal solid waste comprises the putrescible materials, paper, and plastic and averages 80% of the total municipal solid waste collected. Municipal solid waste can be converted into energy by direct combustion, or by natural anaerobic digestion in the engineered landfill. At the landfill sites, the gas produced by the natural decomposition of municipal solid waste (approximately 50% methane and 50% carbon dioxide) is collected from the stored material and scrubbed and cleaned before feeding into internal combustion engines or gas turbines to generate heat and power. The organic fraction of municipal solid waste can be anaerobically stabilized in a high-rate digester to obtain biogas for electricity or steam generation.

Sewage is a source of biomass energy that is similar to the other animal wastes. Energy can be extracted from sewage using anaerobic digestion to produce biogas. The sewage sludge that remains can be incinerated or undergo pyrolysis to produce more biogas.

See also: Biogas, Biomass, Municipal Solid Waste, Waste.

Bio-oil

Bio-oil (sometimes called bio-crude) is the liquid condensate produced from biomass (forestry residues, crop residues, waste paper, and organic waste) by means of processes such as pyrolysis (thermal and catalytic). Depending on the feedstock, the bio-oil could be compatible with existing refinery technology and can be converted into fuels, such as gasoline, diesel fuel, and jet fuel.

The product can vary from a light tarry material to a free-flowing liquid that is produced by the thermal decomposition (destructive distillation) of biomass at temperatures on the order of 400°C (750°F) (Table B-25).

Table B-25 Examples of the yield of bio-oil by pyrolysis from agricultural residues at different temperatures (°C).

Sample	400	450	500	550	600	650	700	775
Hazelnut shell	38.0	39.5	40.4	41.9	42.2	41.0	39.2	38.5
Tea waste	34.9	35.8	36.0	36.2	38.0	37.0	35.5	33.4
Tobacco stalk	41.0	41.8	43.0	40.2	40.0	40.6	37.3	36.8

Also, the product is of interest as a possible complement (eventually a substitute) to crude oil to produce specification-grade fuels (Table B-26).

Table B-26 Representation of the conversion of biomass into fuels.

Process	Product	Process	Refinery
Pyrolysis			
	Bio-oil	Deoxygenation	
			Gasoline
			Diesel
			Jet fuel

Bio-oil is not a product of thermodynamic equilibrium during pyrolysis but is produced with short reactor times and rapid cooling or quenching from the pyrolysis temperatures. Bio-oils are multi-component mixtures of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose, and lignin. Bio-oil is a liquid mixture of oxygenated compounds containing carbonyl, carboxyl, and phenolic functional groups. One of the main drawbacks of the bio-oil is that the composition of the pyrolytic oils is similar to that of the original biomass and is different from crude oil-derived fuels and chemicals (Maher and Bressler, 2007).

Hydrocarbon moieties are predominant in the product, but the presence of varying levels of oxygen (depending upon the character of the feedstock) requires treatment (using for example, hydrotreating) during refining. On the other hand, the bio-oil can be used as a feedstock to the Fischer-Tropsch process for the production of lower-boiling products, as is the case when naphtha and gas oil are used as feedstocks for the Fischer-Tropsch process. In summary, the Fischer-Tropsch process produces hydrocarbon products of different molecular weight from a gas mixture of carbon monoxide and hydrogen (synthesis gas) all of which can find use in various energy scenarios.

In the hydrothermal upgrading process (HTU process), biomass is treated with water at high temperature (300 to 350°C, 570 to 660°F) and pressure 1,770 to 2,650 psi) to produce bio-crude. This can be separated by flashing or by extraction to a viscous oil that is suitable for co-combustion in coal power stations and low-density crude oil, which can be upgraded by hydrodeoxygenation (HDO) to biofuels.

The rapid thermal processing process (RTP™ process) occurs at a temperature of approximately 500°C (930°F), when a turbulent stream of hot sand flashes the biomass into a vapor. The vapor is then rapidly condensed into a liquid. This process occurs in less than two seconds, yielding high quantities of bio-oil (typically 65 to 75% w/w yield of pyrolysis oil from dried lignocellulosic biomass).

Bio-oil is a dark brown viscous liquid that bears some resemblance to fossil crude oil. However, bio-oil is a complex oxygenated compound comprised of water, water-soluble compounds, such as acid derivatives, ester derivative, and water-insoluble compounds, usually called pyrolytic lignin because it comes from the lignin fraction of the biomass. The elemental composition of bio-oil is similar to that of the parent biomass. Because of its high oxygen content, the heating value (Btu per gallon) of bio-oil is lower than fossil fuel, typically only approximately half the heating value of fossil crude such as high-boiling fuel oil. However, it contains less nitrogen and only traces of metals or sulfur.

Bio-oil is acidic with a pH in the 2-4 range, making it highly unstable and corrosive – the acidity can be lessened by the addition of readily available base compounds. It, therefore, presents transportation/piping and storage challenges including the tendency to corrode most metals. Hence, it is usually transported and stored in stainless steel containers. Generally, the properties of bio-oil are variable (Table B-27) and dependent on the feedstock. The specific gravity of the liquid is approximately 1.10 to 1.25, which means it is slightly heavier than water, heavier than fuel oil, and significantly heavier than the bulk density of the original biomass. The viscosity of the oil varies from as low as 25 cP up to 1,000 cP, depending on the water content and the original feedstock.

Table B-27 Typical properties and composition of bio-oil*.

Property	
Water content, % w/w	15 – 35
pH	2.8 – 4.0
Density (kg/L)	1.1 - 1.25
Elemental analysis (moisture free)	
Carbon, % w/w	55 – 64
Hydrogen, % w/w	5 – 8
Nitrogen, % w/w	0.05 – 1
Sulfur, % w/w	0 - 0.05
Oxygen, % w/w	100 - (C + H + N + S)
Ash, % w/w	0.03 - 0.3
Viscosity (42°C, 108°F, cP)	25-1000

*Also called *pyrolysis oil*.

Although freshly made bio-oil can be pumped and transported through pipelines, its viscosity increases with time. Unprocessed bio-oil cannot be readily mixed with crude oil-derived fuels.

Despite the above-mentioned shortcomings, bio-oil has great potential. It can be used as heating oil if proper furnaces can be designed to do so; nitrogen oxide emissions are low when combusted. Additionally, it can be potentially upgraded (or refined) to produce liquid transportation fuels and organic chemicals.

Due to large amounts of oxygenated components present in bio-oil, the oil tends to be polar (like water) and, therefore, does not mix readily with hydrocarbon derivatives or with biodiesel. The degradation products from the biomass constituents include organic acids (like formic and acetic acid), giving the oil its low pH, typically between 2 and 4. Water is also an integral part of the single-phase chemical solution (water-soluble fraction).

The water content of bio-oil is typically 15 to 35% v/v, and the oil has the tendency to phase-separate when the water content reaches the 30 to 45% v/v range. The heating value (i.e., the higher heating value, HHV) is below 11,175 Btu/lb compared to 18,052-18,911 Btu/lb for conventional fuel oils. The high heating values of bio-oil (dry-ash free) of switchgrass (cave-in-rock), corn cob, corn stover (no cobs) and alfalfa stems at early bud are 10,164, 11,249, 10,448, and 14,249 Btu/lb, respectively.

See also: Biomass, Bio-oil Upgrading, Fischer-Tropsch Process, Hydrothermal Upgrading Process.

Bio-oil – Upgrading

Bio-oil produced by the pyrolysis of lignocellulosic materials is among the most complex and inexpensive raw oils that can be derived from biomass and required upgrading prior to use. Typically, bio-oil consists of five major fractions: (i) water, 15 to 30% w/w, (ii) low-boiling oxygenated compounds, 8 to 26% w/w, (iii) phenols derivatives, 2 to 7% w/w, (iv) water-insoluble oligomers derived from lignin, 15 to 25% w/w, and (v) water-soluble products, 10 to 30% w/w.

Upgrading bio-oil to a conventional transport fuel such as gasoline, diesel, gasoline, methane, or liquefied petroleum gas (LPG) requires water removal, deoxygenation (by hydrocracking and/or hydrotreating), followed by product recovery (typically by distillation), which can be accomplished by integrated conventional refinery processes (Table B-28).

Table B-28 Simplified illustration of bio-oil upgrading.

Feedstock	Process (primary)	Product	Process (secondary)	Products
Biomass	Pyrolysis*	Bio-oil		
			Hydrocracking	
			(plus hydrotreating)	Methane
				Naphtha (gasoline)
				Kerosene (diesel)
			Gasification	
			(synthesis gas)	Alcohols
				Hydrocarbons

*Often referred to as thermal cracking in the refining industry.

There is also interest in partial upgrading to a product that is compatible with refinery streams in order to take advantage of the economy of scale and experience in a conventional refinery. Integration into refineries by upgrading through cracking or hydrotreating is a viable option, but in such cases where the bio-oil is blended with a crude oil product, there may be incompatibility issues that arise.

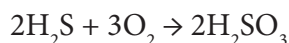
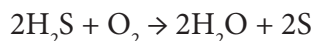
Upgrading bio-oil to a conventional transport fuel such as diesel, gasoline, kerosene, methane, and liquefied petroleum gas (LPG) requires full deoxygenation and conventional refining, which can be accomplished either by integrated catalytic pyrolysis or by decoupled liquid phase hydrodeoxygenation. There is also growing interest in partial upgrading to a product that is compatible with refinery streams in order to take advantage of the economy of scale and experience in a conventional refinery, and the main methods are: (i) hydrodeoxygenation and (ii) catalytic cracking, in situ or ex situ gasification to synthesis gas followed by synthesis to hydrocarbon derivatives or alcohol derivatives.

Hydrothermal liquefaction under a hot-water environment has been proposed as an alternative process to provide better energy efficiency and unique characteristics of bio-oil and other related products compared to pyrolysis-based processes. The optimization of the operating parameters, including temperature, pressure, time, and catalyst, is crucial for improving the performance of these processes. In addition to bio-oil production technologies, several upgrading technologies based on catalytic approaches (e.g., hydrotreatment and esterification) have also been developed to further improve bio-oil quality for a variety of applications.

See also: Bio-oil, Refining.

Bio-oxidation

Bio-oxidation (biological oxidation) is one of the most used methods of desulfurization, based on injection of a small amount of air (2 to 8% v/v) into the raw gas stream. This way, the hydrogen sulfide is biologically oxidized either to solid free sulfur or to liquid sulfurous acid (H_2SO_3):



In practice, the precipitated sulfur is collected and added to the storage tanks where it is mixed with digestate, in order to improve the fertilizer properties of digestate. Biological desulfurization is frequently carried out inside the digester, and, for this kind of desulfurization, oxygen and *Sulfobacter oxydans* bacteria must be present, to convert hydrogen sulfide into elementary sulfur, in the presence of oxygen. Typically, *Sulfobacter oxydans* is present inside the digester (does not have to be added) as the anaerobic digester substrate contains the necessary nutrients for their metabolism. In the process, the air is injected directly in the headspace of the digester and the reactions occur in the reactor headspace, on the floating layer (if existing) and on reactor walls. Due to the acidic nature of the products, there is the risk of corrosion. The process is dependent of the existence of a stable floating layer inside the digester, and the process often takes place in a separate reactor.

Chemical desulfurization of gas streams can take place outside of digester, using a base (usually sodium hydroxide). Another chemical method to reduce the content of hydrogen sulfide is to add commercial ferrous solution (Fe^{2+}) to the feedstock. Ferrous compounds bind sulfur in an insoluble compound in the liquid phase, thereby preventing the production of gaseous hydrogen sulfide.

See also: Biofiltration, Bioscrubbing, Gas Cleaning – Biological Methods Gas Processing, Gas Treating.

Biophotolysis

The photosynthetic production of gas (e.g., hydrogen) hydrogen employs microorganisms such as cyanobacteria, which have been genetically modified to produce pure hydrogen rather than the metabolically relevant substances. The conversion efficiency from sunlight to hydrogen is small, usually under 0.1%, indicating the need for large collection areas.

The current thinking favors ocean locations of the bio-reactors. They have to float on the surface (due to rapidly decreasing solar radiation as function of depth), and they have to be closed entities with a transparent surface (e.g., glass), in order that the hydrogen produced is retained and in order for sunlight to reach the bacteria. Because hydrogen buildup hinders further production, there further has to be a continuous removal of the hydrogen produced, by pipelines to, for example, a shore location, where gas treatment and purification can take place. These requirements make it little likely that equipment cost can be kept so low that the low efficiency can be tolerated.

A further problem is that if the bacteria are modified to produce maximum hydrogen, their own growth and reproduction are quenched. Presumably, there has to be made a compromise between the requirements of the organism and the amount of hydrogen produced for export, so that replacement of organisms (produced at some central biofactory) does not have to be made at frequent intervals. The implication of this is probably an overall efficiency lower than 0.05%.

In a life-cycle assessment of bio-hydrogen produced by photosynthesis, the impacts from equipment manufacture are likely substantial. To this, one should add the risks involved in production of large amounts of genetically modified organisms. In conventional agriculture, it is claimed that such negative impacts can be limited, because of the slow spreading of genetically modified organisms to new locations (by wind or by vectors such as insects, birds, or other animals).

In the case of ocean bio-hydrogen farming, the unavoidable breaking of some of the glass- or transparent plastic-covered panels will allow the genetically modified organisms to spread over the ocean involved and ultimately the entire biosphere. A quantitative discussion of such risks is difficult, but the negative cost prospects of the bio-hydrogen scheme probably rule out any practical use anyway.

Biopower

Biopower (biomass power, renewable electric energy) is the use of biomass feedstock to produce electric power or heat through direct combustion of the feedstock, through biopower system technologies (such as: direct-firing, co-firing, gasification, pyrolysis, and anaerobic digestion), gasification and then combustion of the resultant

gas, or through other thermal conversion processes. Power is generated with engines, turbines, fuel cells, or other equipment.

Most biopower plants use direct-fired systems. They burn bioenergy feedstocks directly to produce steam. This steam drives a turbine, which turns a generator that converts the power into electricity. In some biomass industries, the spent steam from the power plant is also used for manufacturing processes or to heat buildings. Such combined heat and power systems greatly increase overall energy efficiency. Paper mills, the largest current producers of biomass power, generate electricity or process heat as part of the process for recovering pulping chemicals.

Co-firing refers to mixing biomass with fossil fuels in conventional power plants. Coal-fired power plants can use co-firing systems to significantly reduce emissions, especially sulfur dioxide emissions. Gasification systems use high temperatures and an oxygen-starved environment to convert biomass into synthesis gas, a mixture of hydrogen and carbon monoxide. The synthesis gas (syngas) can be converted into other fuels or products, burned in a conventional boiler, or used instead of natural gas in a gas turbine. Gas turbines are very much like jet engines, only they turn electric generators instead of propelling a jet. Highly efficient to begin with, they can be made to operate in a “combined cycle,” in which their exhaust gases are used to boil water for steam, a second round of power generation, and even higher efficiency.

Using a similar thermochemical process but different conditions (totally excluding rather than limiting oxygen, in a simplified sense) will pyrolyze biomass to a liquid rather than gasify it. As with syngas, pyrolysis oil can be burned to generate electricity or used as a chemical source for making plastics, adhesives, or other bioproducts.

The natural decay of biomass produces methane, which can be captured and used for power production. In landfills, wells can be drilled to release the methane from decaying organic matter. Then, pipes from each well carry the methane to a central point, where it is filtered and cleaned before burning. This produces electricity and reduces the release of methane (a very potent greenhouse gas) into the atmosphere.

Methane can also be produced from biomass through a process called anaerobic digestion. Natural consortia of bacteria are used to decompose organic matter in the absence of oxygen in closed reactors. Gas suitable for power production is produced, and possibly troublesome wastes (such as those at sewage treatment plants or feedlots) are turned to usable compost.

Gasification, anaerobic digestion, and other biomass power technologies can be used in small, modular systems with internal combustion or other generators. These could be helpful for providing electrical power to villages remote from the electrical grid—particularly if they can use the waste heat for crop drying or other local industries. Small, modular systems can also fit well with distributed energy generation systems.

See also: Bioenergy, Biofuels, Biomass to Energy.

Bioprocess

A bioprocess is any process that uses complete living cells or organisms or their components (e.g., bacteria, enzymes) to effect desired a physical change and/or a chemical change in the feedstock. Transport of energy and mass is fundamental to many biological and environmental processes.

Modern bioprocess technology used this principle and is actually an extension of older methods for developing useful products by taking advantage of natural biological activities. Although more sophisticated, modern bioprocess technology is based on the same principle: combining living matter (whole organisms or enzymes) with nutrients under the conditions necessary to make the desired end product. Bioprocesses have become widely used in several fields of commercial biotechnology, such as production of enzymes (used, for example, in food processing and waste management) and antibiotics.

Since bioprocesses use living material, they offer several advantages over conventional chemical methods of production. Bioprocesses usually require lower temperature, pressure, and pH (the measure of acidity) and can use renewable resources (biomass) as raw materials. In addition, greater quantities can be produced with less energy consumption.

In most bioprocesses, enzymes are used to catalyze the biochemical reactions of whole microorganisms or their cellular components. The biological catalyst causes the reactions to occur but is not changed. After a series of such reactions (which take place in large vessels (fermenters or fermentation tanks), the initial raw materials are

chemically changed to form the desired end product. Nevertheless, there are challenges to the use of bioprocesses in the production of synthetic fuels.

First, the conditions under which the reactions occur must be rigidly maintained. Temperature, pressure, pH, oxygen content, and flow rate are some of the process parameters that must be kept at specific levels. With the development of automated and computerized equipment, it is becoming much easier to accurately monitor reaction conditions and thus increase production efficiency.

Second, the reactions can result in the formation of many unwanted by-products. The presence of contaminating waste material often poses a two-fold problem related to (i) the means to recover (or separate) the end product in a way that leaves as little residue as possible in the catalytic system, and (ii) the means by which the desired product can be isolated in pure form.

See also: Bioconversion Platform.

Bioreactor

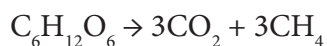
One of the major areas of research concerning landfill is the use of bioreactors. A bioreactor is formed under specific land filling conditions. Bioreactor land filling is a process in which water and air are circulated into a specially-designed landfill, in order to cause accelerated biological decomposition of the waste material. The intention for this type of landfill operation is to maximize the generation of biogas, which is captured using a network of perforated pipes and burnt to generate electricity. Another desired outcome is the rapid stabilization of organic waste material (in order to minimize the length of time required to manage the landfill site or to make use of the decomposed material as compost).

By adding and recirculating liquids in bioreactors, decomposition is accelerated under anaerobic conditions, increasing the production of landfill gas by 2 to 10 times, approximately half of which is methane with at least 23 times the warming potential as carbon dioxide. The result is to shift substantial volumes of methane production, which otherwise would not occur for decades hence, to the present.

In the landfill, which acts as a bioreactor, anaerobic digestion occurs insofar as the naturally occurring processes of anaerobic degradation are harnessed and contained. Anaerobic digestion has a long history dating back to the 10th century BC and involves four stages which are (i) hydrolysis, (ii) acidogenesis, (iii) acetogenesis, and (iv) methanogenesis. These stages result from the biological treatment of organic waste by two key bacterial groups – acetogens, and methanogens.

The hydrolysis stage is the chemical reaction where complex organic molecules are broken down into simple sugars, amino acids, and fatty acids with the addition of hydroxyl groups. The acidogenesis stage is the process where a further breakdown by acidogens into simpler molecules, volatile fatty acids occurs, producing ammonia, carbon dioxide, and hydrogen sulfide as by-products. The acetogenesis stage is the biochemical process where the simple molecules from acidogenesis are further digested by acetogens to produce carbon dioxide, hydrogen, and mainly acetic acid. The methanogenesis fourth stage is the biochemical process where methane, carbon dioxide, and water are produced by methanogens.

A simplified overall chemical reaction for the degradation of sugars produced by the hydrolysis of cellulose is:



Thus, the desirable product of the landfill bioreactor is methane. Other products may (depending upon the composition of the waste material in the landfill) include (i) a solid fibrous material, which is spread without further treatment, or after post composting (maturation), to provide organic matter for improvement of soil quality and fertility (improves soil structure and reduces summer irrigation demand) and (ii) a liquid fraction which contains nutrients and can be spread as a fertilizer and sprayed on crops. If the solid and liquid fractions are not separated, the slurry can be spread on the soil.

Effective gas generation in bioreactors under saturated conditions of rapid differential settlement without a low permeable cover is impossible. The result of this practice, which significantly increases early gas generation without effective gas capture, is a significant near-term increase of potent greenhouse gas emissions into the atmosphere.

The use of clay caps and advanced liner systems and bentonite is useful for the prevention of leachate and landfill gas release, but a consequence of this is that moisture, which is required for the biodegradative processes, is often excluded. The result of this is that much of the waste can remain intact entombed inside the landfill, potentially for longer than the lifetime of the barriers. One method to reduce this effect, by enhancing and accelerating waste stabilization, is to operate the landfill as a bioreactor. The bioreactor landfill attempts to control, monitor, and optimize the waste stabilization process rather than contain the wastes as prescribed by most regulations. This is carried out in an aerobic environment as opposed to the normal situation in landfill sites, where conditions within the wastes are commonly anaerobic.

The future of the bioreactor may well be found in its use with an anaerobic system i.e., a hybrid arrangement. For example, air could be added to the anaerobic processes after the degradation of waste has occurred, thus removing excess moisture from the landfill and fully composting the waste. The cycling of both conditions (aerobic and anaerobic) also offers the possibility of treating a greater range of chemicals such as the nitrification and denitrification of ammonia.

See also: Anaerobic Digestion, Landfill Gas.

Biorefinery

A biorefinery is the means by which biomass can be converted to other products using a biochemical platform or a thermochemical platform which can be simply represented (Table B-29). Thus:

Table B-29 Simplified representation of a biorefinery.

Feedstock	Platform	Intermediate feedstock	Products
Biomass			
	Biochemical		
		Sugars	
			Fuels
			Chemicals
		Residues	
			Heat
			Power
	Thermochemical		
		Gas	
			Heat
			Power
			Fuels
			Chemicals
		Liquids	
			Fuels
			Chemicals

In the current context, the other products are biofuels which have the potential to replace certain crude oil-derived fuels. Thus, biorefining offers a key method to accessing the integrated production of chemicals, materials, and fuels. The biorefinery concept is analogous to that of an oil refinery except that biomass (instead of crude oil) is the feedstock to the refinery.

Biomass refers to (i) energy crops grown specifically to be used as fuel, such as fast-growing trees or switch grass, (ii) agricultural residues and by-products, such as straw, sugarcane fiber, and rice hulls, and (iii) residues from forestry, construction, and other wood-processing industries. These products can range from biomaterials to fuels such as ethanol or important feedstocks for the production of chemicals and other materials.

Biomass is a renewable energy source, unlike the fossil fuel resources (natural gas, crude oil, and coal) and, like the fossil fuels, biomass is a form of stored solar energy but produced in lesser time than the fossil fuels. Thus, a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The concept is based on the modern crude oil refinery concept, which produces multiple fuels and products from crude oil. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry.

Plants are effective chemical mini-factories or refineries insofar as they produce chemicals by specific pathways. The chemicals they produce are usually essential manufacture (called metabolites) which include sugars and amino acids that are essential for the growth of the plant, as well as more complex compounds.

In a manner similar to the crude oil refinery, a biorefinery would integrate a variety of conversion processes to produce multiple product streams such as motor fuels and other chemicals from biomass (Table B-30). In short, a biorefinery would combine the essential technologies to transform biological raw materials into a range of industrially useful intermediates. However, the type of biorefinery would have to be differentiated by the character of the feedstock.

Table B-30 Simplified representation of a biorefinery.

Feedstock	Process (primary)	Products (intermediates)	Process (final)	Products
Biomass	Gasification	Heat		
		Power generation		
	Gas cleaning	Hydrogen		
	Synthesis gas		Fischer-Tropsch	Fuels
	Pretreatment	Cellulose	Hydrolysis	Sugars
Cellulose*	Hydrolysis	Sugars	Fermentation	Ethanol
				Bioproducts
				Chemicals

*Processes for the conversion of lignocellulose and lignin would also be included.

For example, the crop biorefinery would use raw materials such as cereals or maize and the lignocellulose biorefinery would use raw material with high cellulose content, such as straw, wood, and paper waste.

In addition, a variety of methods and techniques can be employed to obtain different product portfolios of bulk chemicals, fuels, and materials. Biotechnology-based conversion processes can be used to ferment the biomass carbohydrate content into sugars that can then be further processed. As one example, the fermentation path to lactic acid shows promise as a route to bio-degradable plastics. An alternative is to employ thermochemical conversion processes which use pyrolysis or gasification of biomass to produce a hydrogen-rich synthesis gas which can be used in a wide range of chemical processes. Thus, a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to the crude oil refinery, which produce multiple fuels and products from crude oil.

A biorefinery can have different options for the production of biofuels from wood and other biomass materials. There is the (i) bioconversion, (ii) thermal conversion, and (iii) thermochemical conversion. Each of these options has merits, but selection is dependent on the feedstock and the desired product slate.

By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume, liquid transportation fuel, while generating electricity and processing heat for its own use and perhaps enough for the sale of electricity. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions.

As a feedstock, biomass can be converted by thermal or biological routes to a wide range of useful forms of energy including process heat, steam, electricity, as well as liquid fuels, chemicals, and synthesis gas. As a raw material, biomass is a nearly universal feedstock due to its versatility, domestic availability, and renewable character. At the same time, it also has its limitations. For example, the energy density of biomass is low compared to that of coal, liquid crude oil, or crude oil-derived fuels. The heat content of biomass, on a dry basis (7,000 to 9,000 Btu/lb) is at best comparable with that of a low-rank coal or lignite, and substantially (50 to 100%) lower than that of anthracite, most bituminous coals, and crude oil. Most biomass, as received, has a high burden of physically adsorbed moisture, up to 50% by weight. Thus, without substantial drying, the energy content of a biomass feed per unit mass is even less.

These inherent characteristics and limitations of biomass feedstocks have focused the development of efficient methods of chemically transforming and upgrading biomass feedstocks in a refinery. The refinery would be based on two “platforms” to promote different product slates.

The sugar-base involves the breakdown of biomass into raw component sugars using chemical and biological means. The raw fuels may then be upgraded to produce fuels and chemicals that are interchangeable with existing commodities such as transportation fuels, oils, and hydrogen.

Although a number of new bioprocesses have been commercialized, it is clear that economic and technical barriers still exist before the full potential of this area can be realized. One concept gaining considerable momentum is the biorefinery which could significantly reduce production costs of plant-based chemicals and facilitate their substitution into existing markets. This concept is analogous to that of a modern oil refinery in that the biorefinery is a highly integrated complex that will efficiently separate biomass raw materials into individual components and convert these into marketable products such as energy, fuels, and chemicals.

By analogy with crude oil, every element of the plant feedstock will be utilized including the low-value lignin components. However, the different compositional nature of the biomass feedstock, compared to crude oil, will require the application of a wider variety of processing tools in the biorefinery. Processing of the individual components will utilize conventional thermochemical operations and state-of-the-art bioprocessing techniques. The production of biofuels in the biorefinery complex will service existing high-volume markets, providing economy-of-scale benefits and large volumes of by-product streams at minimal cost for upgrading to valuable chemicals. A pertinent example of this is the glycerol by-product produced in biodiesel plants. Glycerol has high functionality and is a potential platform chemical for conversion into a range of higher value chemicals. The high volume product streams in a biorefinery need not necessarily be a fuel but could also be a large-volume chemical intermediate such as ethylene or lactic acid.

A key requirement for delivery of the biorefinery concept is the ability to develop a process technology that can economically access and convert the five and six membered ring sugars present in the cellulose and hemicellulose fractions of the lignocellulosic feedstock. Although engineering technology exists to effectively separate the sugar containing fractions from the lignocellulose, the enzyme technology to economically convert the five ring sugars to useful products requires further development.

The construction of both large biofuel and renewable chemical production facilities coupled with the pace at which bioscience is being both developed and applied demonstrates that the utilization of non-food crops will become more significant in the near term. The biorefinery concept provides a means to significantly reduce production costs such that a substantial substitution of petrochemicals by renewable chemicals becomes possible. However, significant technical challenges remain before the biorefinery concept can be realized.

See also: Bioconversion, Bioconversion Platform, Biomass, Refining, Thermal Conversion, Thermal Conversion Platform.

Bio-SCOT Process

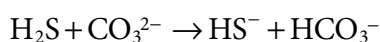
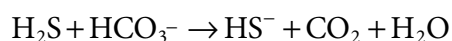
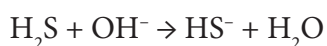
The Bio-SCOT process is a combination of the SCOT and Shell-Paques processes. This process can reduce the sulfur emissions from the sulfur recovery facilities to a low level thanks to the higher efficiency of the scrubber in the Shell-Paques technology.

The process eliminates the need to recycle hydrogen sulfide back to the inlet of the Claus unit. The hydrogen sulfide is converted to solid elemental sulfur in the form of a slurry, which can be melted and mixed with the sulphur from the Claus unit.

See also: Biodesulfurization, SCOT Process, Tail Gas Cleaning.

Bioscrubbing

Bioscrubber systems have been used for hydrogen sulfide removal from gas streams. The bioscrubber involves a two-stage process with an absorption tower and a bioreactor, in which the sulfide is oxidized to sulfur and/or sulfate. For example, the Shell-Paques THIOPAQ® process employs alkaline conditions to produce elemental sulfur. In the first step of this process, the hydrogen sulfide is absorbed into an alkaline solution by reaction with hydroxyl and bicarbonate ions. In the second step, the hydrosulfide is oxidized to elemental sulfur under oxygen-limiting conditions. Thus:



See also: Biofiltration, Bio-oxidation, Gas Cleaning – Biological Methods Gas Processing, Gas Treating.

Bitumen

The term bitumen (also, on occasion, referred to as native asphalt, and extra heavy oil) includes a wide variety of reddish-brown to black materials of semisolid, viscous to brittle character that can exist in nature with no mineral impurity or with mineral matter contents that exceed 50% by weight. Bitumen is frequently found filling pores and crevices of sandstone, limestone, or argillaceous sediments, in which case the organic and associated mineral matrix is known as rock asphalt.

Bitumen is a naturally-occurring material that is found in deposits where the permeability is low and passage of fluids through the deposit can only be achieved by prior application of fracturing techniques. Tar sand bitumen is a high-boiling material with little, if any, material boiling below 350°C (660°F), and the boiling range approximates the boiling range of an atmospheric residuum.

In order to define bitumen, extra heavy oil, heavy oil, and conventional crude oil, the use of a single physical parameter such as viscosity is not sufficient. Physical properties such as API gravity, elemental analysis, and composition fall short of giving an adequate definition. It is the properties of the bulk deposit and, most of all, the necessary recovery methods that form the basis of the definition of these materials. Only then is it possible to classify crude oil, heavy crude oil, extra heavy crude oil, and tar sand bitumen. For example, *tar sands* have been defined in the United States (FE-76-4) as:

...the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques. The hydrocarbon-bearing rocks are variously known as bitumen-rocks oil, impregnated rocks, oil sands, and rock asphalt.

The recovery of the bitumen depends to a large degree on the composition and construction of the sands. Generally, the bitumen found in tar sand deposits is an extremely viscous material that is *immobile under reservoir conditions* and cannot be recovered through a well by the application of secondary or enhanced recovery techniques.

The expression *tar sand* is commonly used in the crude oil industry to describe sandstone reservoirs that are impregnated with a heavy, viscous black crude oil that cannot be retrieved through a well by conventional production techniques (FE-76-4, above). However, the term *tar sand* is actually a misnomer; more correctly, the name *tar* is usually applied to the heavy product remaining after the destructive distillation of coal or other organic matter. Thus, alternative names, such as *bituminous sand* or *oil sand*, are gradually finding usage, with the former name (bituminous sands) more technically correct. The term *oil sand* is also used in the same way as the term *tar sand*, and these terms are often used interchangeably.

On an international note, the bitumen in tar sand deposits represents a potentially large supply of energy. However, many of the reserves are available only with some difficulty and that optional refinery scenarios will be necessary for conversion of these materials to liquid products because of the substantial differences in character between conventional crude oil and tar sand bitumen.

Because of the diversity of available information and the continuing attempts to delineate the various world tar sand deposits, it is virtually impossible to present accurate numbers that reflect the extent of the reserves in terms of the barrel unit. Indeed, investigations into the extent of many of the world's deposits are continuing at such a rate that the numbers vary from one year to the next.

The term *bitumen*, as used in oil shale technology is the lower molecular weight soluble, organic component of oil shale. The amount of bitumen is low, usually on the order of 0.5 to 5% w/w of the total weight of the oil shale. Thus, oil shale organic matter can be characterized as two materials, kerogen and bitumen, the latter being benzene soluble. Bitumen is also the product produced by the high molecular weight material thermal decomposition of kerogen.

The yield of bitumen (extractable material) increases with (i) increasing extraction temperature, (ii) with increasing polarity of the extraction solvent, and (iii) with the chemical reactivity of the solvent. Moreover, bitumen is generally richer in hydrogen (H/C may be on the order of approximately 1.6 with a molecular weight of approximately 1,200) and nitrogen, while it is lower in the proportion of aromatic constituents (and consequently richer in aliphatic constituents) than the corresponding kerogen.

Although the thermal decomposition kinetics is complex, the thermal decomposition of the bitumen (either extracted or produced from the thermal decomposition of kerogen) is often simply described (like the thermal decomposition of kerogen) by a kinetic mechanism involving a first order mechanism which involves the production of *thermal bitumen*:



Black Liquor

Black liquor is the solution of lignin-residue and the pulping chemicals from the Kraft process which is used to extract lignin during the manufacture of paper. The black liquor is an aqueous solution of lignin residues, hemicellulose, and the inorganic chemicals used in the process and contains more than half of the energy content of the wood fed into the digester. Black liquor (Table B-19) is typically concentrated to 65 to 80% by multi-effect evaporators and burned in a recovery boiler to produce energy and recover the cooking chemicals.

The gasification of black liquor has the potential to achieve higher overall energy efficiency while generating an energy-rich synthesis gas. The synthesis gas can be burned in a gas turbine combined cycle system or converted through Fischer-Tropsch chemistry into chemicals or fuels such as methanol, dimethyl ether (DME), gasoline, or diesel.

See also: Dimethyl Ether, Fischer-Tropsch, Methanol.

Blended Fuels

Blended fuel usually refers to a mixture composed of automotive gasoline and another liquid, other than a minimal amount of a product such as carburetor detergent or oxidation inhibitor, which can be used as a fuel in a motor vehicle.

Typically, in the current sense of the term, a blended fuel is a mixture of traditional fuels (such as gasoline or diesel fuel) and alternative fuels (such as ethanol or biodiesel, respectively) in varying percentages. The lowest-percentage blends are being marketed and introduced to work with current technologies while paving the way for future integration. For example, B5 and B20 (diesel fuel blended with 5% or a 20%, respectively of a biofuel) can be pumped directly into the tank of any diesel-fueled vehicle. Ethanol is also blended (approximately 10% v/v) into much of the gasoline dispensed in many countries, especially in metropolitan areas, to reduce emissions.

The use of blended fuels is part of the transition to using more alternative fuels. Although the pure alcohol (methanol or ethanol) will burn independently, cold weather starting can be a problem. An engine has to be designed exclusively for a particular fuel to take advantage of all the characteristics of that fuel. Without the infrastructure in place to support pure alcohol fuels, flex-fuel vehicles (FFVs) have been designed to run on both alcohol and gasoline. The flex-fuel vehicles join the best characteristics of both methanol and gasoline (or ethanol and gasoline) and make it possible to utilize higher blend percentages such as E85 (ethanol) and M85 (methanol). Examples of blended fuels are presented below.

E10

E10 is a low-level blend composed of 10% ethanol and 90% gasoline that has been approved by the United States Environmental Protection Agency (EPA) for use in any conventional, gasoline-powered vehicle. The use of E10 was spurred by the Clean Air Act Amendment of 1990 (and subsequent laws), which mandated the sale of oxygenated fuels in areas with unhealthy levels of carbon monoxide. Currently, the E10 fuel is sold in every state.

E15

E15 is a low-level blend composed of 10.5 to 15% v/v ethanol and gasoline and is approved for use in newer light-duty conventional vehicles. Stations must adhere to several EPA requirements and regulations when selling E15.

E85

E85 (or flex fuel) is an ethanol-gasoline blend containing 51 to 83% v/v ethanol, depending on geography and season that qualifies as an alternative that can be used in flexible fuel vehicles (FFVs), which have an internal combustion engine and are designed to run on E85, gasoline, or any blend of gasoline and ethanol up to 83% v/v.

See also: Alcohol Blended Fuels, E85.

Blending

Blending is a process which, in the current context, mixes the constituents of the fuel in such a manner as to ensure that there is a homogeneous mixture of all of the ingredients. The process can be carried out numerous times within a fuel manufacturing process when new excipients need to be added to the blend. Fuels as produced at the end of the process are actually blends of different streams since no one unit can, for example, produce specification-grade gasoline or diesel fuel. Thus, blending is the final operation in fuel production.

Blending consists of mixing the products in various proportions to meet specifications such as vapor pressure, specific gravity, sulfur content, viscosity, octane number, cetane index, initial boiling point, and pour point. Blending can be carried out in-line or in batch blending tanks. Air emissions from blending are fugitive volatile organic compounds (VOCs) from blending tanks, valves, pumps, and mixing operations. During the blending process, not only the physical and chemical properties of each blending component have to be considered in order to produce the specification-grade fuel and ensure that instability or incompatibility do not occur.

In fact, the major refinery products produced by the product blending process are gasoline, jet fuels, heating oils, and diesel fuels. The objective of product blending is to allocate the available blending components in such a way as

to ensure all product demands and specifications are met at the least cost and to produce products which maximize overall profit. Gasoline blending is a refinery operation that blends different component streams into various grades of gasoline. Typical grades include 83 octane (blended later with an oxygenated fuel such as ethanol), regular 87 octane, and premium 92 octane. The Reid Vapor Pressure (RVP) is set depending on the average temperature of the location the gasoline will be used (cold temperatures require higher RVP than warmer climates). These two specifications are the most significant, and they are documented with each blend, to minimize the potential for octane giveaway.

Most refiners use computer-controlled in-line blending for blending gasoline and distillates. Inventories of blending stocks, together with cost and physical property data, are maintained in a database. Many of the properties of blend components are non-linear, such as octane number, so estimating final blend properties from the components can be quite complex. When a certain volume of a given quality product is specified, the computer uses linear programming models (LP's) to optimize the blending operations to select the blending components to produce the required volume of the specified product.

See also: Blended Fuels.

Blue Gas

Blue gas is a mixture of gases and consists predominantly of carbon monoxide and hydrogen formed by action of steam on hot coal or coke. The mixture has a tendency to burn with a blue flame, hence the name of the gas.

See also: Blue Water Gas, Carbureted Blue Gas.

Blue Water Gas

Blue water gas (sometimes referred to as blue gas) is produced in a similar manner to produce gas but allows the production of a higher heat content gas by intermittent blasting the incandescent bed with air and steam such that the overall heat balance is maintained. The products of the air blast contain the nitrogen which reduces heat content of the product gas.

The process follows the similar principles to the production of producer gas with the exception that the problem of nitrogen dilution is overcome. The feedstock bed is simultaneously blasted with air followed by steam – the air reaction is exothermic causing the bed to increase in temperature, and this is balanced by the endothermic reaction of the steam. The typical composition of the product gas is on the order of carbon dioxide 5% v/v, carbon monoxide 41% v/v, hydrogen 49%, v/v, methane 1% v/v, and nitrogen 4% v/v. If oxygen is used instead of air, the process can be continuous and coke is preferred to coal because coal can continue to devolatilize in the blow period thereby reducing process efficiency – there are also issues related to process efficiency that arise from the use of caking coal as the feedstock.

The blue water gas may be enriched by adding a carburetor in which heavy (high density, high-boiling) fuel oil is sprayed into a brick lined chamber during the blow period of the blue water gas plant with air. During the make period, the air is turned off and the oil is cracked into smaller hydrocarbon derivatives in the now-heated chamber. This produces a mixture of hydrocarbon derivatives (predominantly methane) which increases the heat content and enriches the gas product.

See also: Blue Gas.

Boiler Slag

Boiler slag is a by-product produced from a wet-bottom boiler, which is a special type of boiler designed to keep bottom ash in a molten state before it is removed. These types of boilers (slag-tap and cyclone boilers) are much more compact than pulverized coal boilers used by most large utility generating stations and can burn a wide range of fuels and generate a higher proportion of bottom ash than fly ash (50 to 80% w/w bottom ash compared to 15 to 20% w/w bottom ash for pulverized coal boilers). With wet-bottom boilers, the molten ash is withdrawn from the boiler and allowed to flow into quenching water. The rapid cooling of the slag causes it to immediately crystallize into

a black, dense, fine-grained glassy mass that fractures into angular particles, which can be crushed and screened to the appropriate sizes for several uses.

There are two types of wet-bottom boilers: (i) the slag-tap boiler and (ii) the cyclone boiler. The slag-tap boiler burns pulverized coal, and the cyclone boiler burns crushed coal. In each type, the bottom ash is kept in a molten state and tapped off as a liquid. Both boiler types have a solid base with an orifice that can be opened to permit the molten ash that has collected at the base to flow into the ash hopper below. The ash hopper in wet-bottom furnaces contains quenching water. When the molten slag comes in contact with the quenching water, it fractures instantly, crystallizes, and forms pellets. The resulting boiler slag, often referred to as *black beauty*, is a coarse, hard, black, angular, glassy material.

Since boiler slag is angular, dense, and hard, it is often used as a wear-resistant component in surface coatings of asphalt in road paving. Finer-sized boiler slag can be used as blasting grit and is commonly used for coating roofing shingles. Other uses include raw material for the manufacture of cement and in colder climates; it is spread onto icy roads for traction control. Because there are so many uses and such a limited supply, most of the boiler slag produced in the United States is used and some even imported from other countries.

See also: Ash, Biomass Ash.

Boiling Water Reactor

A boiling water reactor (BWR) is a type of light (H_2O and not HDO or D_2O in which hydrogen has been replaced by deuterium) water nuclear reactor used for the generation of electrical power.

The steam in boiling water reactor is produced directly in the reactor core, while, in contact, the steam in a pressurized water reactor (PWR) is produced in a secondary system. The pressure of a pressurized boiling reactor varies from the primary system to the output steam, while the pressure of a boiling water reactor remains constant.

An advantage of the pressurized water reactor is that the pressurized water reactor can operate at higher temperature and pressure on the order of approximately 315°C (600°F) and 2,400 psi. This provides a higher efficiency than the boiling water reactor.

See: Nuclear Reactor – Boiling Water Reactor.

Bone Dry

The term bone dry when applied to biomass or a biomass product refers to 0% moisture content and refers to (in this context) the biomass being extremely or completely dry. For example, wood heated in an oven at a constant temperature of 100°C (212°F) or above until its weight stabilizes is considered bone dry or oven dry.

Boson

A boson is a particle which carries a force and has a whole number spin (spin is a property of subatomic particles). Bosons carry energy. A photon is an example of a boson as it has a spin of 1 and carries electromagnetism. Mesons are also bosons as they carry nuclear force.

See also: Electron, Nuclear Energy, Photon, Positron.

Bottom Ash

The most common type of furnace in the electric utility industry is the dry, bottom- pulverized feedstock boiler. When pulverized feedstock is burned in a dry, bottom boiler, approximately 80% w/w of the unburned material or ash is entrained in the flue gas and is captured and recovered as fly ash. The remaining 20% w/w of the ash is dry bottom ash, a dark gray, granular, porous solid that is collected in a water-filled hopper at the bottom of the furnace.

When a sufficient amount of bottom ash drops into the hopper, it is removed by means of high-pressure water jets and conveyed by sluiceways, either to a disposal pond or to a decant basin for dewatering, crushing, and stockpiling for disposal or use.

Bottom ash is the coarser component of the ash and may comprise a substantial portion of the waste. Rather than floating into the exhaust stacks, it settles to the bottom of the power plant boiler. Bottom ash is not quite as useful as fly ash, although power plant owners have tried to develop options for beneficial use options, such as structural fill and road-base material. However, the bottom ash remains toxic when recycled and can leak heavy metals into the groundwater.

See also: Ash, Biomass Ash, Boiler Slag, Fly Ash.

Bottoming Cycle

The bottoming cycle is a cogeneration system in which steam is used first for process heat and then for electric power production. In the plant, a waste-heat recovery boiler recaptures the unused energy and uses it to produce steam to drive a steam turbine generator to produce electricity.

Bottoming cycle plants produce high temperature heat for industrial processes, and then a waste heat recovery boiler feeds an electrical plant. These plants are only used when the industrial process requires high temperatures, such as furnaces for glass and metal manufacturing, so they are less common.

Bottom Sediment and Water

Bottom sediment and water (sometimes referred to as basic sediment and water, BS&W) is a both a technical specification of certain impurities in liquid feedstocks and fuels and the method for measuring these properties. In the crude state, many fuels contain water and suspended solids – the particulate matter is also referred to as sediment. The water and solids are measured as BS&W. Considerable importance is attached to the presence of water or sediment in fuels because the water and sediment lead to difficulties in use.

Water, with its dissolved salts, may occur as easily removable suspended droplets or as an emulsion. The sediment dispersed in crude oil may be comprised of inorganic minerals from the production of the fuel as well as scale and rust from pipelines and tanks used for oil transportation and storage. Usually, water is present in far greater amounts than sediment but, collectively, it is unusual for them to exceed 1% of the crude oil on a delivered basis. Water and sediment can foul heaters, stills, and exchangers and can contribute to corrosion and to deleterious product quality. Also, water and sediment are principal components of the sludge that accumulates in storage tanks and must be disposed of periodically in an environmentally acceptable manner. Knowledge of the water and sediment content is also important in accurately determining net volumes of crude oil in sales, taxation, exchanges, and custody transfers.

The sediment consists of finely divided solids that may be drilling mud or sand or scale picked up during the transport of the fuel. The solids may be dispersed in the fuel or carried in water droplets. In any form, water and sediment are highly undesirable in a fuel and the relevant tests involving distillation (ASTM D95, ASTM D4006), centrifuging (ASTM D4007), extraction (ASTM D473), and the Karl Fischer titration (ASTM D4377, ASTM D4928) are regarded as important in fuel quality examinations.

See also: Hot Filtration Test.

Boudouard Reaction

The Boudouard reaction is a gasification reaction in which the carbon dioxide formed reacts with carbon to form carbon monoxide:



The reaction is an endothermic reaction and is favored at high temperatures (680°C, 1255°F). Unlike the gasification reactions, combustion reactions are highly exothermic, so the heat generated in combustion is usually balanced by the steam gasification reaction to attain heat integration. An idealized char gasifier with all inlet and outlet streams is used at the same temperature (i.e., 370°C, 700°F).

Breeder Reactor

A breeder reactor is a type of nuclear reactor which produces more fissile materials than they consume. The reactor is designed to extend the nuclear fuel supply for the generation of electricity, and has even been mistakenly called a potential renewable energy source.

By irradiation of a fissile material such as uranium-238 (^{238}U) or thorium-232 (^{232}Th), the reactor creates more fissile material than is used. Breeder reactors were at first found viable because they made more complete use of uranium fuel than light water reactor. Typically, a breeder reactor creates 30% more fuel than it consumes. After an initial introduction of enriched uranium, the reactor only needs infrequent addition of stable uranium, which is then converted into the fuel.

See: Nuclear Reactor – Breeder Reactor.

BRI Process

The BRI process uses a two-stage gasifier that raises the syngas temperature as high as 1,370 °C (2,500 °F) in the second stage to enable cracking of any high-boiling hydrocarbon derivatives to carbon monoxide and hydrogen, maximizing the ethanol yield, thus using a thermal cracking.

The hot producer gases are cooled to 37°C (98°F), and introduced into the biocatalytic reactor where ethanol is produced. Here, the modified bacteria culture *Clostridium ljungdahlii* is introduced and nutrients are added to provide for cell growth and automatic regeneration of the biocatalyst.

With a hydrogen/carbon monoxide ratio of 2, the reactions indicate that water and ethanol are the only products.

As the ethanol is toxic to the bacteria, there is a need to hold the ethanol concentrations below 3% in the reactor. A dilute, aqueous stream of ethanol is continuously removed through a membrane that retains cells for recycle to maximize reaction rates. Anhydrous ethanol is produced by conventional distillation followed by a molecular sieve, using the waste heat from the process. Water, with nutrients, is recycled from the distillation bottoms back to the biocatalytic reactor. With ambient temperature and pressures, a fermentation time of a few minutes has been achieved.

Briquette

A briquette (or briquet) is a block of carbonaceous smokeless fuel (flammable matter) which is used as fuel to start and maintain a fire. Common types of briquettes are charcoal briquettes and biomass briquettes. Briquettes are used for both domestic and industrial use, prepared from bituminous coal using a binder. Briquette production is a mature technology, and the technology associated with coal briquetting has been developed for almost 100 years.

Historically, briquettes (especially coal and coke briquettes) have been used for fuel for approximately 100 years. Traditionally, briquetting technology was established for developing countries to produce briquettes of local residues, for use in household cooking stoves and restaurants. Later, as the capacities of the machines increased, briquettes were used in industrial boilers to create heat, steam, and power for industry and power plants. Within the past three decades, briquetting has also found its way to households in industrialized countries as consumer logs for wood-burning stoves and fireplaces. However, with the advent of modern fuel systems, the use of briquettes has declined and use for these products is found most often in the operation of barbecue units. While still a marketable product for such use, briquettes as fuel (such as *smokeless fuel*) are not used often for domestic and industrial heating. In more recent years, as the focus on renewable energy has grown, the applications for briquettes have grown concurrently, as have different technologies and new applications.

The briquette has to be ignited from the bottom by burning wood. During ignition, the upper part of briquette, upon heating, emits volatile matter which is a mixture of carbon and hydrogen compounds and is a strong pollutant. The newly developed briquettes can be ignited from the top just by striking a match, and the volatile matter will be burnt away when it has passed the upper flame. The briquette should be coated with a thin layer of combustibles and oxidizing agent and, therefore, should be kept in a dry place lest moisture retards ignition.

See also: Briquette Binder, Briquette Manufacture.

Briquette Binder

The binder used for coal briquetting has considerable influence of the properties of the finished product. Coke-oven tar (or the solid pitch) has been, and continues to be, widely used as a binder in the production of briquettes from bituminous coal, although crude oil-derived products are also being used.

The composition of bituminous coal tar and pitch is complex and consists of a wide variety of components. The coke-forming components of the pitch are of great importance for briquetting, and pitch from low-volatile coal (such as anthracite) has been preferred. These coals do not cake or melt while burning in the furnace; thus, the stability of the briquettes depends entirely on the skeleton of pitch coke formed in the briquette structure. Furthermore, the content of coke-forming components in the tar pitch increases as the rate of pitch distillation is decreased.

Pitch viscosity also exerts a strong influence on the process as do the coal-binder interactions. During the briquetting process, the properties of the binder pitch are changed by heat, duration of the process, air, and steam. These factors can change pitch composition in the thin layer present in the heated briquetting matrix.

Crude oil residua used in the briquetting of coals have often been given the collective name asphalt (*bitumen* in Europe and many other countries). The most important data used to characterize such asphalt is the softening point, the penetration, the Conradson carbon residue, and the plasticity range which indicate the thermoplastic character of the binder and content of coke-forming components.

These two properties are considerably different in asphalt and coal-tar pitch. Crude oil-derived materials have a lower content of coke-forming components than coal-tar pitch, and this may be a disadvantage when crude oil-derived materials are used as binders for noncaking coal briquettes. Use of crude oil-derived materials having a lower than-desirable propensity for coke formation, as indicated by a low Conradson carbon residue, produces briquettes that have a low stability during firing.

Propane asphalt (produced in a crude oil refinery) has a lower penetration value than asphalts obtained by distillation or by oxidation. Propane asphalt has a relatively high temperature sensitivity which may cause the briquettes to adhere more efficiently. It is possible to alter the temperature sensitivity of the propane asphalt by the conventional methods of treatment which are used to alter asphalt properties for highway use.

Sulfite liquor is a by-product obtained during the treatment of wood with sulfites (calcium, sodium, magnesium, and ammonium) to produce cellulose. The liquor has significant adhesion properties thereby fulfilling one of the binder requirements for use as a briquette binder.

The sulfite liquor and the sulfite pitch remaining after water removal are water soluble. Briquettes made with sulfite liquor as the binder can be rendered water-resistant (referred to as *hardening the briquette*) by heating to 220 to 350°C (430 to 660°F).

Slightly sintering or lightly caking coals can be briquetted with calcium sulfite liquor or with magnesium or sodium sulfite liquor as a binder. Briquettes that are stable during firing can be made from anthracite coals only when using ammonium sulfite liquor. This low-ash binder produces a favorable coke skeleton in the briquette structure during combustion.

Starch has a substantial adhesive power, and 1 to 3% w/w starch added to the coal, as a solid or in a suspension, can be used as a binder for the production of coal briquettes. Starch is used in the manufacture of charcoal briquettes, which are used in increasing amounts as barbeque briquettes.

See also: Briquette, Briquette Manufacture.

Briquette Manufacture

Briquette manufacture (also known as briquetting) is undergoing resurgence, principally due to the convergence of three critical factors. In fact, the recent developments in briquette processing and binding have dramatically changed the economics of using fuel briquettes as an energy resource. Also, a shortage of fuel wood has become increasingly severe in most of the developing countries. Finally, there has been a steady increase by environmental concerns to address the problem of domestic and urban waste disposal, a dilemma that briquetting can help remedy.

Generally, briquette manufacture (briquetting) involves the collection of combustible materials that are not usable as such because of their low density, and compressing them into a solid fuel product of any convenient shape that can be burned like wood or charcoal. Thus, the material is compressed to form a product of higher bulk density, lower moisture content, and uniform size, shape, and material properties. Briquettes are easier to package and store, cheaper to transport, more convenient to use, and their burning characteristics are better than those of the original organic waste material.

The raw material of a briquette must bind during compression; otherwise, when the briquette is removed from the mold, it will crumble. Improved cohesion can be obtained with a binder but also without, since under high temperature and pressure, some materials such as wood bind naturally. A binder must not cause smoke or gummy deposits, while the creation of excess dust must also be avoided. Two different sorts of binders may be employed. Combustible binders are prepared from natural or synthetic resins, animal manure or treated, dewatered sewage sludge. Non-combustible binders include clay, cement, and other adhesive minerals. Although combustible binders are preferable, non-combustible binders may be suitable if used in sufficiently low concentrations. For example, if organic waste is mixed with too much clay, the briquettes will not easily ignite or burn uniformly. Suitable binders include starch (5 to 10%) or molasses (15 to 25%), although their use can prove expensive. It is important to identify additional, inexpensive materials to serve as briquette binders and the optimum concentrations of the materials. The exact method of preparation depends upon the material being briquetted but, in general, the overall process can be presented as a step-wise operation: Thus:

Collection

Drying

Size reduction

Binder addition

Briquetting

Drying

Sales

See also: Briquette, Briquette Binder, Briquette Properties, Briquetting Processes.

Briquette Properties

The shape and the size of briquettes depend essentially on their application. Briquettes for industrial use are usually cubes or bricks weighing 1 to 4 lbs. The briquettes manufactured for domestic use must be small enough to be loaded conveniently through the appliance filling aperture but not small enough to drop through the grate bars or to give high resistance to air flow, even in deep beds.

There are few, if any, recognized specifications or standard tests available for measuring the mechanical properties of bituminous coal briquettes. The properties currently measured are the breaking strengths and the abrasion or attrition of the briquettes. The attrition testing of briquettes by means of the tumbler tests permits the comparison of briquettes that have the same weight but different shapes (breaking or crushing strengths of briquettes that vary in shape cannot be compared). The test involves placing the briquette between two parallel plates and loading one plate until the briquette breaks. The larger the surface of contact between the testing plate and the briquette, the larger the point compressive strength.

The thermal post-treatment of the briquettes at different temperatures, with or without the influence of oxygen in the air, leads to briquettes which (depending on the feed material, the treatment method, and the treatment temperature) have properties more or less similar to those of coke. The briquettes undergo carbonization in one of several steps. The thermal post-treatment depends on the type of briquettes being treated and the desired properties of the final product. Heating rate and residence time in the hot zone are the deciding factors; however, the composition properties of the raw briquettes also influence the processing steps and the nature of the final product.

If the binder pitch softens, the briquettes may be deformed, or glued together as a result of the exuding of binder from the briquette surface. Such difficulties are avoided by an oxidative hardening pretreatment or by maintaining the briquettes in a quiescent state during the temperature interval used for binder softening.

The most important data used to characterize briquette binders are the softening point, the penetration, the carbon residue, and the plasticity range. These data indicate the thermoplastic behavior of the binder and content of coke-forming components. These two properties are considerably different in bitumens and coal-tar pitches. For example, crude oil-derived materials have a lower content of coke-forming components than coal-tar pitch, and this may be a disadvantage when crude oil-derived materials are used as binders for noncaking coal briquettes, especially of anthracites. Use of crude oil-derived materials having a lower-than-desirable propensity for coke formation, as indicated by a low Conradson carbon residue, produces briquettes that have a low stability during firing.

The use of propane asphalt as a briquette binder has also been investigated; propane asphalt is the propane-insoluble portion of crude oil residua. The asphalt has a lower penetration value than asphalts obtained by distillation or by oxidation. Propane asphalt has a relatively high temperature sensitivity which may cause the briquettes to stick together. It is possible to alter the temperature sensitivity of the propane asphalt by the conventional methods of treatment which are used to alter asphalt properties for highway use.

See also: Briquette, Briquette Binder, Briquette Manufacture, Briquetting Processes.

Briquetting Processes

The processes available for the production of briquettes are many and, often, not too varied. The production of coal briquettes is closely related to the carbonization process by which fuel-grade coke is produced. In fact, briquettes are manufactured from coals that are normally considered to be of insufficient quality to produce coke. A non-caking coal having a low content of volatile matter might be briquetted with a binder at 750 to 800°C (1,380 to 1,470°F).

A recent emphasis on the use of coal is the production of added-value products using a variety of processes by which the total coal can be used with little wastage of the products. Such is the character of the mild gasification process and a variety of other clean coal processes which have brought related to renewed interest in briquetting and pelletization of coal.

The mild gasification process is a modification of the conventional coal gasification and produces gaseous, liquid, and solid products by heating coal in an oxygen-free reactor. The process is less of a gasification process and more of a pyrolysis process insofar as volatile matter is removed by thermal means to leave a carbonaceous char/residue. The char can be upgraded further to remove both ash and pyritic sulfur, mixed back with coal-derived liquids, and burned in both coal- and oil-fired boilers.

The process is of interest since a slurry of the liquid fuel and the upgraded char has the potential of being a very versatile fuel that can be burned in both coal- and oil-fired boilers. If the char is upgraded to a high degree, even feedstock coal with a high sulfur content can be used without alternating heat rates or capacity factors.

The production of briquettes (and/or pellets) from coal is a thermal decomposition process, akin to the carbonization process.

Carbonization is essentially a thermal treatment process for the production of a carbonaceous residue (with the simultaneous removal of distillate) from a variety of organic substances:



The process may also be referred to as destructive distillation and has been applied to a range of organic materials, but more particularly to naturally-occurring materials such as wood, sugar, and vegetable matter. The carbonaceous residue from the thermal decomposition of coal is usually referred to as coke (which is physically dissimilar from charcoal) and has the more familiar honeycomb-type structure.

The thermal decomposition of the carbonaceous feedstock is a complex sequence of events which can be described in terms of several important physicochemical changes, such as the tendency of the feedstock to soften and flow when heated or the relationship to carbon-type in the feedstock. In fact, some feedstocks become quite fluid at temperatures of the order of 400 to 500°C (750 to 930°F) and there is a considerable variation in the degree of maximum plasticity, the temperature of maximum plasticity, as well as the plasticity temperature range for some feedstocks. Significant changes also occur in the structure of the char during the various stages of devolatilization.

A briquetting plant typically consists of the mixer-dryer with drive, the fan, and the gas ducts. From the mixing chamber, flue gas at 300 to 500°C (570 to 930°F) passes through the coal-binder mixture, suction being provided by the fan. After cooling, the material enters roll presses from the mixer-dryer.

Water, among other factors, influences the wetting and adhesion between coal and bituminous binder and on the strength of the resultant briquette. Indeed, interfacial interactions between the coal and the binder are extremely important in determining the strength of the briquette. The moisture content of the feedstock, before the addition of the bituminous binder, should be as low as possible, preferably not exceeding 4% w/w.

See also: Briquette, Briquette Binder, Briquette Manufacture, Briquette Properties.

Bromine Number

The bromine number is used as a method of determining the unsaturation in typical hydrocarbon molecules.

The bromine number is the number of grams of bromine absorbed by 100 g of oil which indicates the percentage of double bonds in the material. The number is an indicator of the unsaturated constituents in a liquid fuel. In the test method, a known weight of the sample dissolved in a specified solvent maintained at 0 to 5°C (32 to 41°F) is titrated with standard bromide-bromate solution. However, the determination of the end point is method dependent.

BTEX

BTEX is an acronym that stands for benzene, toluene, ethylbenzene, and xylenes that occur in the lower-boiling liquid fuels (Figure B-3). These compounds are some of the volatile organic compounds (VOCs) found in crude oil derivatives such as gasoline.

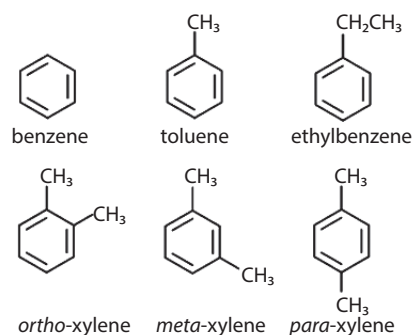


Figure B-3 Constituents of the BTEX Mixture.

Toluene, ethylbenzene, and xylenes have harmful effects on the central nervous system. BTEX compounds are notorious due to the contamination of soil and groundwater, which typically occurs near crude oil and natural gas production sites, and petrol stations and other areas with underground storage tanks (USTs) or above-ground storage tanks (ASTs) containing gasoline or other crude oil-related products.

The analysis for the BTEX group is performed using a purge and trap device which, owing to differences in volatility and water insolubility, easily separates the BTEX group from the complex sample matrix. In addition, the analytes are identified with a photo-ionization detector (PID) which responds selectively to aromatic hydrocarbon derivatives while showing only a small or negative response to paraffin derivatives, oxygenated hydrocarbon derivatives, and other components of the gas stream. Hence, the BTEX analysis is not only one of the most commonly requested, but also a fairly simple, straightforward method.

See also: BTX.

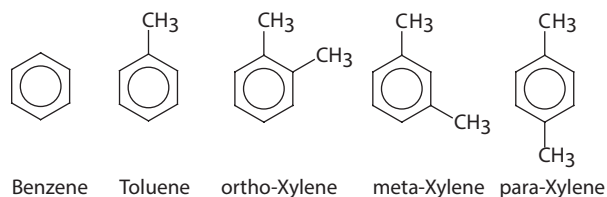
BTU

The Btu (British thermal unit) is a unit of measurement for energy and is the amount of heat that is necessary to raise the temperature of one pound of water by 1 degree, Fahrenheit.

BTX

BTX is an acronym for benzene, toluene, and xylene, which are components of the lower-boiling liquid fuels.

Benzene, the simplest aromatic, is carcinogenic, and its level in gasoline is severely restricted. Toluene and xylene have benzene rings which are attached to one or two methyl (CH_3) groups, respectively; xylene has three isomers, with the methyl groups adjacent on the ring (ortho), separated by one carbon (meta), or separated by two carbons (para):



See also: BTEX.

Bubble Point

The bubble point is the temperature at which incipient vaporization of a liquid in a liquid mixture occurs, corresponding with the equilibrium point of 0% vaporization or 100% condensation. The bubble point is based on the fact that liquid is held in the pores of the filter by surface tension and capillary forces. The minimum pressure required to force liquid out of the pores is a measure of the pore diameter. The pressure required to force liquid out of a liquid-filled capillary must be sufficient to overcome surface tension and is a direct measure of an effective tube diameter.

The *bubble point pressure* (P_b) is the pressure at which saturation will occur in the liquid phase (for a given temperature) and is the point at which vapor (bubble) first starts to come out of the liquid (due to pressure depletion). The bubble point temperature is usually lower than the dew point temperature for a given mixture at a given pressure.

Since the vapor above a liquid will probably have a different composition to the liquid, the bubble point (along with the *dew point*) data at different compositions are useful data when designing distillation systems and for constructing phase diagrams as a means of studying phase relationships. As pressures are reduced below the bubble point, the relative volume of the gas phase increases. For pressures above the bubble point, a crude oil is said to be undersaturated. At or below the bubble point, the crude is saturated.

A bubble point test is a test method that is designed to determine the pressure at which a continuous stream of bubbles is initially seen downstream of a wetted filter under gas pressure. The bubble point test is a practical,

nondestructive test used for estimating the pore size of microporous filters and confirming the integrity of sterilizing membrane filters and filter systems. It is the most widely used non-destructive integrity test.

To perform a *bubble point test*, gas is applied to one side of a wetted filter, with the tubing downstream of the filter submerged in a bucket of water. The filter must be wetted uniformly such that water fills all the voids within the filter media. When gas pressure is applied to one side of the membrane, the test gas will dissolve into the water, to an extent determined by the solubility of the gas in water. Downstream of the filter, the pressure is lower. Therefore, the gas in the water on the downstream side is driven out of solution. As the applied upstream gas pressure is increased, the diffusive flow downstream increases proportionally. At some point, the pressure becomes great enough to expel the water from one or more passageways establishing a path for the bulk flow of air. As a result, a steady stream of bubbles should be seen exiting the submerged tubing. The pressure at which this steady stream is noticed is referred to as the bubble point.

Bubbling Fluidized Bed Gasifier

A bubbling fluidized bed (BFB) consists of fine, inert particles of sand or alumina, which are selected based on their suitability of physical properties such as size, density, and thermal characteristics. The gas flow rate is chosen to maintain the bed in a fluidization condition, which enters at the bottom of the vessel.

The dimension of the bed at some height above the distributor plate is increased to reduce the superficial gas velocity below the fluidization velocity to maintain inventory of solids and to act as a disengaging zone. A cyclone is used to trap the smaller size particle that exit the fluidized bed, either to return fines to the bed or to remove ash rich fines from the system.

Biomass is introduced either through a feed chute to the top of the bed or deep inside the bed. The deeper introduction of biomass in to the bed of inert solids provides sufficient residence time for fines that would otherwise be entrained in the fluidizing gas. The biomass organics pyrolytically vaporize and are partially combusted in the bed. The exothermic combustion provides the heat to maintain the bed at temperature and to volatilize additional biomass.

The bed needs to be preheated to the startup temperature using hydrocarbon resources such as natural gas, fuel oil, either by direct firing or by indirect heating. After the bed reaches the biomass ignition temperature, biomass is slowly introduced into the bed to raise the bed temperature to the desired operating temperature which is normally in the range of 700 to 900°C (1,290 to 1,650°F). Bed temperature is governed by the desire to obtain complete devolatilization versus the need to maintain the bed temperature below the biomass ash fusion temperature. The advantages of the fluidized bed gasifiers are (i) yield of a uniform product gas, (ii) able to accept wide range of fuel particles sizes, including fines, (iii) a near-uniform temperature distribution throughout the reactor, and (iv) a high rate of heat transfer between inert material and biomass, aiding high conversion, with low tar. The disadvantage is formation of large bubbles at higher gas velocities, which bypass the bed reducing the high rate of heat /mass transfer significantly.

See also: Biomass – Gasification.

Bulk Density

The bulk density is the mass of an assembly of coal particles in a container divided by the volume of the container, assuming that the container is full and represents the volume occupied by the solid. The bulk density depends on true density, particle size and size distribution, particle shape, surface moisture, and degree of compaction. The parameter is often used in the design of coal handling, transportation, and storage systems.

Bulk density is a property of powders, granules, and other “divided” solids, especially used in reference to coal and similar solids. The total volume includes particle volume, inter-particle void volume, and internal pore volume.

The bulk density is not an intrinsic property of a material; it can change depending on how the material is handled. For example, powdered coal poured into a cylinder will have a particular bulk density, but if the cylinder is disturbed, the coal particles will move and usually settle closer together, resulting in a higher bulk density. For this

reason, the bulk density of powders is usually reported both as freely settled and tapped density – the tapped density refers to the bulk density of the coal powder after a specified compaction process, usually involving vibration of the container.

The test method (ASTM D291) for determining bulk density concerns the compaction of crushed coal to determine either its compacted or uncompacted weight, for purposes such as charging coke ovens. In addition to the character of the coal itself, moisture content and size distribution of the coal are the two main factors that affect the cubic foot weight. A moisture determination and sieve analysis of the coal should be reported along with the cubic foot weight for proper interpretation of the cubic foot weight. During the period of collecting the gross sample, the increments of the sample shall be stored in a waterproof container with a tightly fitting cover in order to prevent the loss of moisture.

The bulk density differs widely between different types of biomass. Together with the heating value, it determines the energy density of the gasifier feedstock, i.e., the potential energy available per unit volume of the feedstock. Biomass of low bulk density is expensive to handle, transport, and store. Apart from handling and storing behavior, the bulk density is important for the performance of the biomass as a fuel inside the reactor: a high void space tends to result in channeling, bridging, incomplete conversion and a decrease in the capacity of the gasifier. The bulk density varies widely (100 to 1,000 kg/m³) between different biomass feedstocks not only because of the character of the biomass but also as a result of the way the biomass comes available (chips, loose, baled).

Bunker

A bunker is a storage tank used for gaseous fuels, liquid fuels, and biomass fuel products.

Fuel bunkers, commonly known as bunkers, are containers for the storage of fuel on steam-powered boats or steam tank engines or rooms for the storage of fuel in furnaces. The term bunker or fuel bunker is typically only used for storage areas for solid fuels (such as coal or, in the current context, solid biofuel). The term fuel tank is typically used for liquid fuels) or gaseous fuels.

Bunker Fuel Oil

Bunker fuel is technically any type of fuel oil used aboard ships. It gets its name from the containers on ships and in ports that it is stored in; in the days of steam, they were coal bunkers, but now, they are bunker-fuel tanks.

Bunker fuel is the colloquial term for fuel oil used by marine vessels. Bunker fuels A, B, and C are respectively downgrading quality-classifications of fuel oil, characterized by their boiling points, carbon-chain lengths, and viscosities, all of which contribute to their value (in other words, Bunker A is more valuable than Bunker C). Currently, most of the global shipping fleet relies on diesel Bunker C fuel oil which contributes significant amounts of greenhouse gas emissions, sulfur, and other emissions that contribute negatively to climate change and negative environmental and human health impacts.

More specifically, bunker A is No. 2 fuel oil, bunker B is No. 4 or No. 5, and bunker C is No. 6. Since No. 6 is the most common, bunker fuel is often used as a synonym for No. 6. No. 5 fuel oil is also called navy special fuel oil or just navy special, No. 6 or 5 are also called furnace fuel oil (FFO); the high viscosity requires heating, usually by a recirculated low pressure steam system, before the oil can be pumped from a bunker tank. In the context of shipping, the labeling of bunkers as previously described is rarely used in modern practice.

Butane

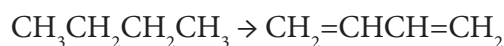
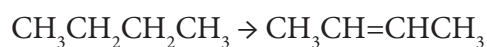
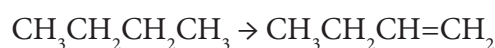
Butane is a gaseous component of natural gas. Butane can also be produced from crude oil. Butane gas (n-butane) is the four-carbon unbranched alkane (CH₃CH₂CH₂CH₃). Butane is also used as a collective term for n-butane together with its only other isomer, iso-butane [methylpropane, CH(CH₃)₃]. Butanes are highly flammable, colorless, odorless, easily liquefied gases.

Butane is sold bottled as a fuel for cooking and camping. When blended with propane and limited amounts of other hydrocarbon derivatives (subject to the specifications), it is referred to commercially as liquefied petroleum gas. It is also used as a gasoline component and as a feedstock for the production of base petrochemicals in steam cracking, as well as a propellant in aerosol sprays.

Very pure forms of butane, especially iso-butane, can be used as refrigerants and have largely replaced the ozone layer-depleting halomethanes in household refrigerators and freezers. The flammability of butane is not usually an issue because the amount of butane in an appliance is not enough to cause a combustible mix given the amount of air in a room.

Butane Dehydrogenation

The *butane dehydrogenation process* is a process for removing hydrogen from butane to produce butenes and, on occasion, butadiene.



This process is achieved in several ways – the most common method is to heat hydrocarbon derivatives to high temperature, as in thermal cracking, that causes some dehydrogenation. In the chemical process industries, nickel, cobalt, platinum, palladium, and mixtures containing potassium, chromium, copper, aluminum, and other metals are used in very large-scale dehydrogenation processes.

n-Butane, iso-butane, and t-butane, while naturally occurring, have few commercial applications beyond fuels. Butanes can be isomerized and then reacted with iso-butene or other light olefins in alkylation processes to yield high-octane motor gasoline blending stock. Butenes, 1-butene, cis-2-butene, trans-2-butene, and iso-butene, also known as butylenes, by comparison have a variety of commercial uses. Iso-butene is a primary reactant in the production of methyl tertiary butyl ether (MTBE), a major additive in reformulated gasoline and used to reduce emissions from automobile exhaust. Butenes are oligomerized and hydrogenated to produce higher alkanes for gasoline blend stock uses and can be reacted further to produce other commercially important products. It is estimated that 90% of butene consumption is in motor fuel applications such as alkylate, polymer gasoline, and oligomerized gasoline blend stocks. Butenes are also blended directly into gasoline and mixed with propane and butanes in liquefied petroleum gas. Approximately 10% of the available butenes are used in chemical production where the most important products are butadiene, sec-butyl alcohol, butyl rubber, and polybutylene elastomer.

Butenes are produced as by-products of many refinery processes. Due to the huge volumes of crude oil subjected to catalytic cracking, catalytic crackers are the single largest source of mixed butenes that are typically used for MTBE production. Cracking catalysts and conditions are sometimes formulated and selected to especially maximize the production of iso-butene. Steam cracking of olefins is another major source of by-product butenes.

Butenes are dehydrogenated further to produce butadiene. Butadiene is one of three copolymers in abs, acrylonitrile-butadiene-styrene plastic and styrene-butadiene rubber. Dehydrogenation reactions are endothermic, and those of butane and butene are no exception.

One goal of the various processes for producing either butenes or butadiene is to maximize feedstock conversion and simultaneously selectivity to the desired product isomer. For example, while mixed butenes are typically used for MTBE and polygas synthesis, polybutylene production requires higher purity 1-butene. The yield of each isomer is controlled by the reaction conditions employed. The recovered yield is controlled by the downstream separation steps applied to the mixture of product and un-reacted starting materials. The practical result of these sometimes conflicting demands is a wide range of conversion technologies and separation approaches, each more or less optimized for a specific end use application.

Maximization of the conversion of feed to product can be accomplished by reducing the vapor pressure of the products in the reactor. A common practice is to add steam to the reactor. This not only reduces the partial pressure of the products driving the conversion higher; it is typically also utilized to import the needed heat of reaction into the reaction vessel. Steam is used because it can be easily separated from the reactor effluent through condensation. Another approach is to selectively remove one of the products of the reaction from the reactor, in this case the hydrogen.

Hydrogen is removed by oxidation to produce water and also to supply some of the required heat of reaction. The direct addition of small amounts of oxygen into the reactor, typically in a specially designed reaction zone, usually with a catalyst present has been described. The risk with this solution is the indiscriminate reaction of the oxygen with either the reactants or the products.

Another approach is to control the side reactions of products with oxygen is to use a membrane reactor to effectively segregate the reactant and product hydrocarbon molecules from the oxygen hydrogen scavenger. A third approach is to utilize redox agents along with the dehydrogenation catalysts that provide a supply of reactive but not free oxygen for reaction with the product hydrogen. One difficulty with this solution is that the redox agents are reduced and consumed in the process and must be regenerated in a separate processing step.

Butane Vapor-Phase Isomerization

Isomerization applications are to provide additional feedstock for alkylation units or high-octane fractions for gasoline blending. Straight-chain paraffins (*n*-butane) are converted to respective *iso*-compounds by continuous catalytic (aluminum chloride and noble metals) processes. Natural gasoline or light straight-run gasoline can provide feed by first fractionating as a preparatory step. High volumetric yields (>95%) and 40 to 60% conversion per pass are characteristic of the isomerization reaction.

The butane vapor phase isomerization process is a process for isomerizing *n*-butane to *iso*-butane using aluminum chloride catalyst on a granular alumina support and with hydrogen chloride as a promoter. A non-regenerable aluminum chloride catalyst is employed with various carriers in a fixed-bed or liquid contactor. Platinum or other metal catalyst processes utilize a fixed-bed operation and can be regenerable or non-regenerable. The reaction conditions vary widely depending on the particular process and feedstock, 40 to 480°C (100 to 900°F) and 150 to 1,000 psi; residence time in the reactor is 10 to 40 minutes.

The butane vapor phase isomerization process is a process for isomerizing *n*-butane to *iso*-butane using aluminum chloride catalyst on a granular alumina support and with hydrogen chloride as a promoter.

Butanol

Butanol (butyl alcohol) is a four-carbon alcohol that can be obtained by fermentation from the same feedstocks used in ethanol fermentation. Some properties of butanol are superior to ethanol for fuel – butanol has more energy/gallon than ethanol, it does not absorb water easily which unlike ethanol may allow it to be transported via gasoline pipeline, and butanol-gasoline blends have lower vapor pressure than ethanol-gasoline blends which is important in reducing evaporative hydrocarbon emissions. The obvious advantages of butanol are the high octane rating (over 100) and high energy content, only approximately 10% lower than gasoline, and subsequently approximately 50% more energy-dense than ethanol, 100% more so than methanol. The major disadvantage of butanol is the high flash point (35°C, 95°F).

Traditionally, butanol is fermented from *Clostridium acetobutylicum* via the so-called ABE (acetone-butanol-ethanol) fermentation. ABE fermentation yields 3 parts acetone, 6 parts butanol, and 1 part ethanol (3:6:1). However, butanol from ABE fermentation is less economic than ethanol essentially because the fermentation is impeded by low concentrations of the products (end-product inhibition) requiring larger process stream volumes, reactors, and tanks.

See also: Alcohols, Ethanol, Methanol, Propanol.

Butene

Butene, also known as butylene, is an alkene with the formula C_4H_8 ($CH_3CH=CHCH_3$ or $CH_3CH_2CH=CH_2$) (Table B-31). The butene derivatives are colorless gases that are typically obtained by catalytic cracking of long-chain hydrocarbon derivatives during refining of crude oil. Cracking produces a mixture of products, and the butene is extracted from this by fractional distillation.

Table B-31 The defend isomers of butene (C_4H_8).

Common name(s)	Structure
α -butylene, 1-butene	
cis-2-butene, <i>cis</i> - β -butylene	
trans-2-butene, <i>trans</i> - β -butylene	
isobutylene, isobutene	

All four of these isomers are gases at room temperature and pressure but can be liquefied by lowering the temperature or raising the pressure. These gases are colorless, but do have distinct odors and are highly flammable. Although not naturally present in crude oil, they can be produced from by the catalytic cracking of crude oil and higher- molecular-weight crude oil products. Although they are stable compounds, the carbon-carbon double bonds make them more reactive than similar alkane derivatives, which are more inert compounds in various ways. Because of the double bonds, these 4-carbon alkene derivatives can act as monomers in the formation of polymers, as well as having other uses as petrochemical intermediates.

See also: Alkenes.

Butene Dehydrogenation

Butenes, 1-butene, cis-2-butene, trans-2-butene, and iso-butene, also known as butylenes, have a variety of commercial uses. Iso-butene is a primary reactant in the production of methyl tertiary butyl ether (MTBE), a major additive in reformulated gasoline and used to reduce emissions from automobile exhaust. Butenes are oligomerized and hydrogenated to produce higher alkanes for gasoline blend stock uses and can be reacted further to produce other commercially important products. It is estimated that 90% of butene consumption is in motor fuel applications such as alkylate, polymer gasoline, and oligomerized gasoline blend stocks. Butenes are also blended directly into gasoline and mixed with propane and butanes in LPG. Approximately 10% of the available butenes are used in chemical production where the most important products are butadiene, sec-butyl alcohol, butyl rubber, and polybutylene elastomer.

The butene derivatives are produced as by-products of many refinery processes. Due to the huge volumes of crude oil subjected to catalytic cracking, catalytic crackers are the single largest source of mixed butenes that are typically used for MTBE production. Cracking catalysts and conditions are sometimes formulated and selected to especially maximize the production of iso-butene. Steam cracking of olefins is another major source of by-product butenes.

Butenes are dehydrogenated further to produce butadiene. Butadiene is one of three copolymers in acrylonitrile-butadiene-styrene (ABS) plastic and styrene-butadiene (SB) rubber. Dehydrogenation reactions are endothermic, and those of butane and butene are no exception.

One goal of the various processes for producing either butenes or butadiene is to maximize feedstock conversion and simultaneously selectivity to the desired product isomer. For example, while mixed butenes are typically used for MTBE and polygas synthesis, polybutylene production requires higher purity 1-butene. The yield of each isomer is controlled by the reaction conditions employed. The recovered yield is controlled by the downstream separation steps applied to the mixture of product and un-reacted starting materials. The practical result of these sometimes conflicting demands are a wide range of conversion technologies and separation approaches, each more or less optimized for a specific end use application.

Maximization of the conversion of feed to product can be accomplished by reducing the vapor pressure of the products in the reactor. A common practice is to add steam to the reactor. This not only reduces the partial pressure of the products driving the conversion higher; it is typically also utilized to import the needed heat of reaction into the reaction vessel. Steam is used because it can be easily separated from the reactor effluent through condensation. Another approach is to selectively remove one of the products of the reaction from the reactor, in this case the hydrogen.

Hydrogen is removed by oxidation to produce water and also to supply some of the required heat of reaction. The direct addition of small amounts of oxygen into the reactor, typically in a specially designed reaction zone, usually with a catalyst present has been described. The risk with this solution is the indiscriminate reaction of the oxygen with either the reactants or the products.

Another approach is to control the side reactions of products with oxygen is to use a membrane reactor to effectively segregate the reactant and product hydrocarbon molecules from the oxygen hydrogen scavenger. A third approach is to utilize redox agents along with the dehydrogenation catalysts that provide a supply of reactive but not free oxygen for reaction with the product hydrogen. One difficulty with this solution is that the redox agents are reduced and consumed in the process and must be regenerated in a separate processing step.

C₁, C₂, C₃, C₄, C₅ Fractions

A common way of representing fractions containing a preponderance of hydrocarbon derivatives having 1, 2, 3, 4, or 5 carbon atoms, respectively, and without reference to hydrocarbon type.

Calorific Value

The calorific value is a direct indication of the heat content (energy value) of the fuel and represents the combined heats of combustion of the carbon, hydrogen, nitrogen, and sulfur in the organic feedstock and is the gross calorific value with a correction applied if the net calorific value is of interest.

The calorific value is usually expressed as the gross calorific value (GCV) or the higher heating value (HHV) and the net calorific value (NCV) or lower calorific value (LHV). The difference between the gross calorific value and the net calorific value is the latent heat of condensation of the water vapor produced during the combustion process. The gross calorific value assumes that the entire vapor produced during the combustion process is fully condensed. The net calorific value assumes that the water is removed with the combustion products without fully being condensed. To equalize all effects, the calorific value of the fuel should be compared based on the net calorific value basis. The calorific value varies considerably depending on the ash, moisture content, and the molecular type of the substance. The unit is calories per gram, which may be converted to the alternate units (1.8 Btu/lb = 1.0 kcal/kgm = 4.187 kJ/kgm).

The calorific value is neither part of the proximate analysis nor part of the ultimate analysis of a carbonaceous material, but it is, in fact, one of the many physical properties of fuels and, as such, in the present context, the importance of the calorific value as one of the means by which a fuel can be evaluated.

See also: Heat Content.

Camelina

Camelina sativa is a flowering plant in the family Brassicaceae and is usually known in English as camelina, gold-of-pleasure, false flax, wild flax, linseed dodder, German sesame, and Siberian oilseed which is native to Europe and to Central Asian areas. This plant is cultivated as an oilseed crop mainly in Europe and in North America.

Camelina is relatively easy to grow and requires few agricultural inputs compared to other crops. It can establish successfully through broadcast seeding on frozen ground in winter or early spring, even in previous crop stubble. Germination occurs after soil temperatures reach 3°C (38°F). Planting with grain drills works well, but results are generally no better than surface broadcasting when there is adequate moisture on the soil surface.

Camelina is generally grown as a summer annual oilseed crop, but it can be grown as a winter annual in milder climates. It is a short-season crop that matures in 85 to 100 days. The plants grow 1 to 3 feet tall and have branched stems that become woody as they mature, and the leaves are 2 to 3½ inches long, arrow-shaped, and pointed with smooth edges. The crop can be grown in arid conditions, prefers lower humidity levels, does not require significant levels of inputs such as fertilizer, and the oil will produce a high-quality biodiesel. Typical varieties of camelina are approximately 38 to 40% w/w oil. At least two firms are offering contracts to producers with stated goals of achieving two million acres of production.

Camelina oil can be used in both edible and industrial products. There is considerable variation in oilseed content among camelina plants from wild collections and old European varieties, and varieties with higher oilseed content

are under development. Camelina oil is relatively high in omega-3 fatty acids and low in saturated fatty acids. The oil also contains gamma tocopherol (vitamin E), which acts as an antioxidant and increases the stability and shelf life of camelina oil compared to other omega-3 oils.

Biodiesel produced from camelina has a variety of benefits. For example, Camelina-based aviation fuel could save 84% of carbon emissions biodiesel and can be produced from Camelina in large quantities.

See also: Biodiesel, Transesterification.

Canola Oil

Canola is a type of rapeseed that is a member of the Brassica family, which includes broccoli, cabbage, cauliflower, mustard, radish, and turnip. Canola is a popular crop throughout the world because of its variety of uses and the nutritional value compared to competing crops. Canola can be produced in some countries where similar crops are not able to grow because of short growing seasons. In the United States, North Dakota is the leading producer of canola. Canola oil has been increasing its market share in the United States, because of its nutritional advantages compared to other competitive vegetable oils. Although canola oil would primarily move into edible markets, increased acreage for the plant will have positive impacts on the overall vegetable oil supply.

There are a number of steps involved in making biodiesel from the canola crop: (i) the oil is removed from the seed; the seed is crushed for the oil contained within and after the oil is extracted, the by-product is a protein rich meal that can be used by the livestock industry, (ii) the canola oil is placed in the mixer with methanol and potassium hydroxide (KOH) and mixed (iii) the mixture is transferred to the reaction vessel using the air compressor where the mixture is left to chemically react, and the glycerol is removed; (iv) a pneumatic diaphragm pump pushes the now-diesel from the reactor vessel to the first washing tank, where it is washed with a fine spray of water which removes the soaps that have formed as a by-product of the chemical process and allowed to settle, (v) the biodiesel moves to the second washing tank to be washed again, settled, and transferred to the cooker where the biodiesel is heated to 100°C (212°F) to boil off any excess water, and (vi) the biodiesel is then filtered into storage containers.

See also: Biodiesel, Bio-oil, Rapeseed.

Capillary Forces

Capillary forces are the interfacial forces between immiscible fluid phases, resulting in pressure differences between the two phases. Capillary action, capillarity, capillary motion, or wicking is the ability of a substance to draw another substance into it. Such forces occur when the adhesive intermolecular forces between the liquid and a substance are stronger than the cohesive intermolecular forces inside the liquid. The effect causes a concave meniscus to form where the substance is touching a vertical surface. The same effect is what causes porous materials such as sponges to soak up liquids.

Capillary forces act at fluid-air-solid interfaces to minimize the surface energy of the interface. Surface tension or capillary forces scale with the perimeter of the wetted area. In the bulk region of a liquid, cohesive forces between the liquid molecules are balanced and shared with all the neighboring molecules. However, at the surface of the liquid, the molecules are not surrounded by liquid molecules on all sides and exert stronger attractive forces with neighboring molecules on and below the surface.

Surface tension is a consequence of the imbalances in attractive forces between molecules and is related to the decrease in surface energy that results from decreasing surface area. At the surface, a layer forms in which the molecules are strongly bonded, thereby making it harder to penetrate the surface of the liquid than to move submersed objects. Stronger interactions between molecules result in higher values of surface tension, while lower values indicate that the molecules are not interacting as strongly. The dimensions for surface tension are expressed as force per unit length or energy per unit area.

See also: Surface Tension.

Capillary Number

The capillary number (N_c) is the ratio of viscous forces to capillary forces, and equal to viscosity times velocity divided by interfacial tension. A common experimental observation is a relationship between residual oil saturation (S_{or}) and local capillary number (N_c). This relationship is called a capillary desaturation curve (CDC). The capillary number reflects the balance between viscous and capillary forces at the pore scale; viscous forces dominate at high capillary numbers, while capillary forces dominate at low capillary numbers. The capillary number at the pore scale can be defined as:

$$N_c = \frac{\mu v}{\gamma \cos \theta}$$

In this equation, μ is the water viscosity, v is the linear advance rate, γ is the oil-water interfacial tension, and θ is the contact angle.

If the viscous forces acting on the trapped oil exceed the capillary retaining forces, residual oil can be mobilized. This is reflected in CDC curves which show that while S_{or} values are constant at low values of the capillary number, they start to decrease above a certain value of the capillary number termed the critical capillary number.

Capillary Pressure

The capillary pressure is the pressure required to drive a fluid through a pore throat and displace the pore-wetting fluid. As pore throats become smaller, higher capillary pressures are required to displace the pore-wetting fluid. Capillary pressure curves are available that provide information regarding pore throat sorting, relative permeability, and reservoir quality. The size of the pore throat is related to the residual water saturation. Water cut is related to the capillarity and the distance above the oil-water contact. Capillarity is important to waterflood performance.

Carbohydrates

A carbohydrate is an organic compound, consisting only of carbon, hydrogen, and oxygen, with general formula $C_m(H_2O)_n$.

Carbohydrates are divided into four chemical groupings which are (i) monosaccharide derivatives, (ii) disaccharide derivatives, (iii) oligosaccharide derivatives, and (iv) polysaccharide derivatives. In general, the monosaccharides and disaccharides, which are smaller (lower molecular weight) carbohydrates, are commonly referred to as sugars. While the scientific nomenclature of carbohydrates is complex, the names of the monosaccharides and disaccharides very often end in the suffix *ose* – for example, glucose (a monosaccharide) and sucrose (a disaccharide).

The term carbohydrate is a synonym of saccharide, and the saccharides form a large family of natural carbohydrates that fill numerous roles in living things. Polysaccharides, such as starch and glycogen, serve for the storage of energy, and cellulose and chitin serve as structural components in plants and arthropods, respectively. The 5-carbon monosaccharide ribose is an important component of coenzymes such as adenosine triphosphate (ATP) and the backbone of the genetic molecules (ribonucleic acid, RNA). The related deoxyribonucleic acid is a component of DNA.

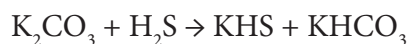
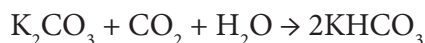
Carbohydrates (starch, cellulose, sugar derivatives) are readily obtained from wheat and potato, while cellulose is obtained from wood pulp. The structures of these polysaccharides can be readily manipulated to produce a range of biodegradable polymers with properties similar to those of conventional plastics such as polystyrene foams and polyethylene film. In addition, these polysaccharides can be hydrolyzed, catalytically or enzymatically to produce sugars, a valuable fermentation feedstock for the production of ethanol, citric acid, lactic acid, and dibasic acids such as succinic acid.

See also: Sugars.

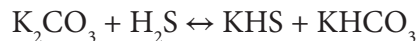
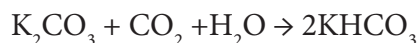
Carbonate Washing and Water Washing

Carbonate washing is a mild alkali process for emission control by the removal of acid gases (such as carbon dioxide and hydrogen sulfide) from gas streams and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature.

The process is at maximum efficiency near the temperature of reversibility of the reactions:



The hot potassium carbonate process employs an aqueous solution of potassium carbonate (K_2CO_3) to remove both carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from gas streams as well as carbonyl sulfide (COS) and carbon disulfide (CS_2), if present.



A high partial pressure of carbon dioxide is required to keep the potassium bicarbonate (KHCO_3) in solution, and hydrogen sulfide will not react if the carbon dioxide pressure is not sufficiently high. The process requires that the absorber and the stripper operate at elevated temperatures in the range of 110 to 115°C (230 to 240°F) – hence the name hot process.

In the process, the sour gas enters at the bottom of the absorber and flows countercurrently to the carbonate liquid stream and the sweet gas exits at the top of the absorber. The rich carbonate solution exits from the bottom of the absorber and is flashed in the stripper, where acid gases are driven off. The lean carbonate solution is pumped back to the absorber. The lean solution may or may not be cooled slightly before entering the absorber.

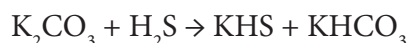
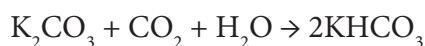
Water washing (water scrubbing), in terms of the outcome, is analogous to washing with potassium carbonate, and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical, and there is also a relatively high absorption of hydrocarbon derivatives, which are liberated at the same time as the acid gases.

Water is also used as an absorbent for gas impurities since it offers some advantages such as (i) water is available at low cost, (ii) water can be used in simple scrubbing units with less concern over leakage than for organic solvents, and (iii) water can be used on a once-through basis, and (iv) water washing does not require heat loads, even if high pumping loads are needed.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Carbonate Washing Process

The hot potassium carbonate process decreases the acid content of natural and refinery gas from as much as 50% to as low as 0.5% and operates in a unit similar to that used for amine treating. The process works best near the temperature of reversibility of the reactions:



The hot potassium carbonate process decreases the acid content of the gas stream from as much as 50% to as low as 0.5% and operates in a unit similar to that used for amine treating. The process using potassium phosphate is

known as phosphate desulfurization, and it is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbon derivatives as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally.

Other processes include the Alkazid process, which removes hydrogen sulfide and carbon dioxide using concentrated aqueous solutions of amino acids. The Giammarco-Vetrocoke process is used for hydrogen sulfide and/or carbon dioxide removal. In the hydrogen sulfide removal section, the reagent consists of sodium or potassium carbonates containing a mixture of arsenite derivatives (such as sodium arsenite, $NaAsO_2$) and arsenate derivatives (such as sodium arsenate, Na_3AsO_4); the carbon dioxide removal section utilizes hot aqueous alkali carbonate solution activated by arsenic trioxide or selenous acid or tellurous acid.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Carbon Cycle

The carbon cycle is a cycle in which carbon is stored in the atmosphere in the form of carbon dioxide, which is absorbed by plants and converted to carbohydrates by the process of photosynthesis. The cycle then follows food chains, with carbohydrates being consumed by herbivores and then carnivores, being metabolized during the process of respiration. Carbon dioxide is returned to the atmosphere as animals exhale and when organic waste and dead organisms decay.

Thus, vegetation and animals are important stores of carbon, although carbon may be rapidly returned to the atmosphere if vegetation is burned. Soils are also important reservoirs for carbon. Atmospheric carbon dioxide is soluble in water, in which it forms carbonic acid, which forms bicarbonate ions and carbonate ions, which in turn form salts (such as the insoluble calcium carbonate, which accumulates in marine sediments, marine organisms, and carbonate rocks, such as limestone). Carbon is typically stored in these forms until it is released to the atmosphere by chemical weathering.

Along with the nitrogen cycle and the water cycle, the carbon cycle comprises a sequence of events that are key to make the Earth capable of sustaining life. The cycle describes the movement of carbon as it is recycled and reused throughout the biosphere, as well as long-term processes of carbon sequestration and release from carbon sinks.

See also: Biogeochemical Cycles, Ecological Cycles.

Carbon Dioxide

Carbon dioxide is a product of combustion that acts as a greenhouse gas in the atmosphere of the Earth, trapping heat and contributing to climate change.

Carbon dioxide is colorless. At low concentrations, the gas is odorless. At higher concentrations, it has a sharp, acidic odor. It will act as an asphyxiant and an irritant. When inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation in the nose and throat. These effects result from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid.

The carbon dioxide molecule ($O=C=O$) contains two double bonds and has a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable. At standard temperature and pressure, the density of carbon dioxide is approximately 1.5 times that of air. Above -78.51°C (-109.3°F), carbon dioxide changes directly from a solid phase to a gaseous phase through sublimation (passing directly into the gas phase leaving no liquid), or from gaseous to solid through deposition. Liquid carbon dioxide forms only at pressures above 75 psi.

See also: Carbon Monoxide.

Carbon Dioxide Balance

The carbon dioxide emissions of fuels can be split into emissions during use and upstream emissions. For oil fuels, the emissions during use are the most important ones. Hydrogen does not result in carbon dioxide emissions during use, and the emissions from biofuels such as ethanol are balanced by the carbon dioxide captured during biomass growth.

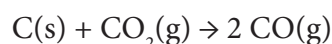
The upstream emissions for many renewable fuels can be substantial. However, for large-scale production processes, carbon dioxide can be captured and stored underground. This can reduce upstream emissions by 85 to 95%. Depending on the primary fuel choice and the combustor, upstream emissions can vary substantially.

Synfuels from gas and coal result in similar emissions to those from crude oil-derived fuels. However, substantial emissions reductions are possible when fuels from biomass and hydrogen from fossil fuels are introduced.

See also: Biofuels, Carbon Dioxide.

Carbon Dioxide Gasification

The reaction of a carbonaceous feedstock (using coal as the example) with carbon dioxide may be approximated or simplified as the reaction of carbon with carbon dioxide, for modeling purpose. Carbon dioxide reacts with carbon to produce carbon monoxide (Boudouard reaction), which is an exothermic reaction:



The reverse reaction is carbon deposition reaction that is a major culprit of carbon fouling on many surfaces, such as process catalyst deactivation. This gasification reaction is thermodynamically favored at high temperatures (>680°C, >1255°F), which is also quite similar to the steam gasification.

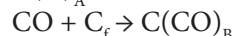
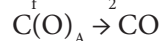
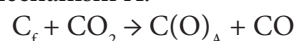
The reaction, if carried out alone, requires high temperature (for fast reaction) and high pressure (for higher reactant concentrations) for significant conversion. However, this reaction in practical gasification application is almost never attempted as a solo chemical reaction, due to a variety of factors such as low conversion, slow kinetic rate, and low thermal efficiency.

There is general agreement that experimental data on the rate of carbon gasification by carbon dioxide fit an empirical equation of the form:

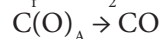
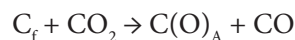
$$r = k_1 p_{\text{CO}_2} / (1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2})$$

In this equation, p_{CO} and p_{CO_2} are partial pressures of CO and CO₂ in the reactor. This rate equation is shown to be consistent with at least two mechanisms where carbon monoxide retards the gasification reaction.

Mechanism A:



Mechanism B:



In both mechanisms, carbon monoxide retards the overall reaction rate. In Mechanism A, retardation occurs via carbon monoxide adsorption onto the free sites, while in Mechanism B, retardation occurs via reaction of chemisorbed oxygen with gaseous carbon monoxide to produce gaseous carbon dioxide.

See also: Carbon Dioxide, Carbon Monoxide.

Carbon Dioxide Recovery

Carbon dioxide recovery processes recover high purity carbon dioxide from gas streams such as boiler flue gases, gas turbine exhausts, and waste gases using absorption/stripping technology to reduce sulfur dioxide levels.

The system is based on absorption/ stripping using a 15% to 20% monoethanolamine (MEA) solution. Feed gases are sent to an amine absorber where they are scrubbed with MEA to recover carbon dioxide. The scrubbed gases are vented to the atmosphere after water washing in the absorbers top to minimize MEA losses. Rich solution from the MEA absorber is preheated in an exchanger, flashed, and sent to stripper where carbon dioxide is recovered overhead. Condensate from the stripper overhead is returned to the system.

Lean mono-ethanolamine from the stripper is cooled, filtered, and returned to the absorber. Periodically, a batch reclaiming operation is conducted to purge mono-ethanolamine degradation products and to recover mono-ethanolamine by decomposing heat-stable salts. The bottoms from the reclaiming operation may be burned as boiler fuel.

Carbon dioxide recovered from the stripper overhead may be compressed and used as a vapor product, or dried and liquefied using a standard ammonia refrigeration system to produce a liquid product.

Operating units have exhibited availability factors in excess of 98%. Absorption and stripping operations take place at slightly above atmospheric pressure. Feed gas can contain up to 15 vol% oxygen, though economics are favored by high carbon dioxide and low oxygen concentrations in the feed. The process can recover carbon dioxide from flue gases containing from 3 to 15 vol% (dry basis) carbon dioxide. Moderate levels of sulfur dioxide and nitrogen oxides in the feed are acceptable. Sulfur dioxide pre-scrubbing is required only with sulfur dioxide levels higher than 100 ppm v/v.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Carbonization

Carbonization is another form of pyrolysis which can convert over one-half of a scrap tire into usable products. Carbonization processes operate at much higher temperatures than typical pyrolysis units. At this higher temperature condition, the main product is char. The char is purified into carbon black, one of the main components in the manufacture of tires.

The carbonization process was originally developed for the production of charcoal from wood and the production of coke from coal. Nevertheless, the process can (and already has) found use in the production of fuels from carbonaceous feedstocks such as biomass.

In the process, the feedstock is converted to carbonaceous volatile products (gases and liquids) and a high-carbon product the removal of volatile materials (gases and condensable liquids, such as bio-oil) and thermal decomposition products (devolatilization) and is usually achieved by the use of temperatures up to 1,500°C (2,730°F). The degradation of the feedstock is severe at these temperatures and produces substantial yields of volatile products, in addition to the high-carbon non-volatile product. The low-temperature carbonization is achieved by the use of temperatures of on the order of 500 to 700°C (930 to 1,290°F) – the temperature range for medium-temperature carbonization processes is self-explanatory.

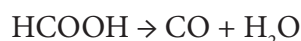
Four main types of products are obtained by low-temperature carbonization processes: (i) gases, (ii) condensable liquids, (iii) tar, and (iv) char. The proportions are determined by the properties and type of feedstock and by the rate and the residence time of the feedstock and the primary products in the hot zone.

Both fluidized-bed and fixed-bed systems have been used; the former system requires direct contact with another heating medium, whereas fixed-bed systems may be heated directly or indirectly. Carriers can vary, and among the carriers for direct heating are steam, air, recycle gases, sand, and metal balls containing a salt to take advantage of the latent heat of fusion. Superheated steam at 540 to 650°C (1,000 to 1,200°F) has been effective. For any particular feedstock, the yield of gases increases with the carbonization temperature while the yield of the solid (char, coke) product decreases. The yields of tar and low-molecular-weight liquids are to some extent variable but are greatly dependent on the process parameters, especially temperature as well as the type of feedstock.

Water has a tendency to reduce the rate of carbonization when certain low-rank coals are employed but is often responsible for increased tar yields. The usual thermal decomposition of the feedstock (i.e., decomposition in the absence of added species) may be markedly influenced by oxidation or by hydrogenation of the feedstock prior to the thermal process; the presence of mineral matter may also be influential.

Carbon Monoxide

Carbon monoxide (CO) is a lethal gas produced by incomplete combustion of carbon-containing fuels in internal combustion engines. The gas is colorless, odorless and tasteless, which is highly toxic to humans and animals. It is the simplest oxo-carbon, and is (chemically) an anhydride of formic acid (HCOOH).



Carbon monoxide is produced from the partial (or incomplete) oxidation of carbon-containing compounds and forms when there is insufficient oxygen to produce carbon dioxide (CO₂). The gas burns with a blue flame, producing carbon dioxide.

Carbon monoxide is one of the most common and widely distributed air pollutants. Carbon monoxide has a slightly lower density than air. In the human body, it reacts readily with hemoglobin to form carboxy-hemoglobin.

See also: Carbon Dioxide.

Carbon Residue

The carbon residue is the amount of carbonaceous residue remaining after thermal decomposition of a carbonaceous fuel or fuel source in a limited amount of air; also called the carbon-forming propensity; also called the Conradson carbon residue or the Ramsbottom carbon residue or the microcarbon residue in reference to the inventor of the respective test methods.

Fuels are mixtures of many compounds that differ widely in their physical and chemical properties. Some of them may be vaporized in the absence of air at atmospheric pressure without leaving an appreciable residue. Other non-volatile compounds leave a carbonaceous residue when destructively distilled under such conditions. This residue is known as carbon residue when it is determined in accordance with a prescribed test procedure.

The carbon residue is a property that can be correlated with several other properties of crude oil; hence, it also presents indications of the volatility of the crude oil and the carbon-forming (or inversely the distillate-producing) propensity. However, tests for carbon residue are sometimes used to evaluate the carbonaceous depositing characteristics of fuels used in certain types of fuel-burning equipment.

The mechanical design and operating conditions of such equipment have such a profound influence on carbon deposition during service that comparison of carbon residues between oils should be considered as giving only a rough approximation of relative deposit-forming tendencies. A more precise relationship between carbon residue and hydrogen content, H/C atomic ratio, nitrogen content, and sulfur content has been shown to exist. These data can provide more precise information related to the anticipated behavior of a variety of feedstocks in thermal processes.

Because of the extremely small values of carbon residue obtained by the Conradson and Ramsbottom methods when applied to the lower-boiling distillate fuel oils, it is customary to distill such products to 10% residual oil and determine the carbon residue thereof. Such values may be used directly in comparing fuel oils, as long as it is kept in mind that the value is that for a residuum and is not to be compared with the carbon residue of the whole feedstock.

See also: Carbonization.

Carbon Sink

A carbon sink is a geographical area whose vegetation and/or soil soak up significant carbon dioxide from the atmosphere. Such areas, typically in tropical regions, are increasingly being sacrificed for energy crop production.

A carbon sink is a reservoir that can absorb or sequester carbon dioxide from the atmosphere and include forests, soils, peat, permafrost, ocean water, and carbonate deposits in the deep ocean. Most of these carbon sinks are large and slow moving; human influence on these sinks is generally deemed fairly minimal, with the possible exception of soils and agriculture.

The most commonly referenced form of carbon sink is that of forests. Plants and trees absorb carbon dioxide from the atmosphere via photosynthesis, retain the carbon component as the building block of plant fiber, and release oxygen back into the atmosphere. Therefore, long-lived, high-biomass plants, such as trees and forests, represent effective carbon sinks as long as they are maintained.

Certain gases, such as chlorofluorocarbons, contribute twofold to climate change by simultaneously trapping reflected heat and thinning the protective ozone layer. This ozone depletion reduces the ability of the atmosphere to absorb and reflect solar radiation. As a result, more solar radiation is able to reach the surface of the Earth and potentially accelerate the process of climate change.

Oceans are also carbon dioxide sinks and represent the largest active carbon sink on Earth, absorbing more than a quarter of the carbon dioxide that humans put into the air.

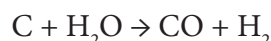
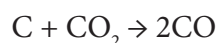
Carbo-V Process

The Carbo-V gasification process presents an innovative and efficient way of converting biomass feedstock into clean, tar-free, and low-methane synthesis gas. Thereby, the three-stage Carbo-V gasification process combines the advantages of an entrained flow gasification originating from coal utilization with an innovative pre-conditioning of the solid biomass which is done by a thermal process (pyrolysis) referred to as low temperature gasification.

In a first process step (the low temperature gasification step), the wood chips are thermally cracked at temperatures between 400 and 500°C (740 and 930°F). The products of this pyrolysis decomposition are charcoal and a pyrolysis gas containing the volatiles components of the wood diluted in the gasification agent. The necessary heat for this pyrolysis process is gained by oxidizing a small amount of the charcoal in the low temperature gasification step. This oxidation is performed by a gasification agent gas which consists of a mixture of oxygen and saturated steam. This mixture is fed to the low temperature gasification step through nozzles at the bottom of the reactor. The char from each low temperature gasification step is cooled, de-compressed to atmospheric pressure, screened, grinded, stored, and then fed to the high temperature gasifier.

In the second process step, the pyrolysis gas as well as the recycled residual coke is further oxidized with pure oxygen in the combustion chamber of the high temperature gasifier at temperatures above the melting point of the fuel ash. Thus, the hydrocarbon-rich pyrolysis gas will be converted to a hydrocarbon-free process gas consisting only of carbon monoxide, carbon dioxide, hydrogen, and steam.

In the third process step, char from the storage silo is fed to the endothermic part of the Carbo-V gasifier via a chamber sluice. The hot process gas from the burning chamber now reacts with the char in the gasification reactor of the high temperature gasifier. Thus:



These reactions are strongly endothermic, and the chemical reactions cool down the gas within the reaction vessel by more than 500°C (930°F). This procedure is also called “chemical quenching” and is one of the major features of the Carbo-V gasification process. It allows keeping a high heating value of the product gas. The crude synthesis gas leaving the high temperature gasifier is now further cooled down to below 200°C via a specially designed gas cooling system. The heat from the gas cooling system is used to produce high pressure steam (up to a maximum of 1,350 psi).

Following the gas cooling system, the crude gas loaded with dust, residual carbon, and the ash components of the feedstock has to be cleaned from solid particles. This occurs in a two-stage de-dusting system. The coarse particles are separated by a gas cyclone followed by a bag house filter system for the fine de-dusting. The residual coke is de-compressed over a chamber sluice and discharged from the system. After grinding of the residual coke to a suitable size, the solid fraction also containing the ash components is fed back to the burner of the high temperature gasifier by a fluidized dense flow steam.

A small portion of the filter dust is removed from the process to prevent the enrichment of impurities in the residual coke circuit. Due to the high gasification temperature in the burning chamber of the high temperature gasifier, the ash components get melted. The melted ash forms a solid layer on the refractory material within the burning chamber which protects the refractory material from thermal stresses, thus permitting long life times of the refractory material. The melted ash trickles down at the wall of the gasifier and is collected in a water basin below the gasifier. In the water basin, the melted ash is rapidly cooled and converted to a slag granulate. The vitrified slag will be periodically discharged from the gasifier over a chamber sluice.

See also: Gasification, Gasification of Biomass

Carbureted Blue Gas

Carbureted blue gas is a mixture of carbon monoxide and hydrogen formed by the action of air and then steam on hot coal or coke and enriched with hydrocarbon gases during its manufacture by a simultaneous process when low-boiling distillate, gas oil, or fuel oil are gasified. The gas has a gross heat content of approximately 500 to 550 Btu/ft³.

See also: Blue Gas, Carbureted Water Gas.

Carbureted Water Gas

Carbureted water gas is the result of combining the water gas and oil gas methods. Briefly, oil gas is the gas formed by the thermal cracking of crude oil. If oil is sprayed onto heated checker work (refractory), it cracks to form lower gaseous hydrocarbon derivatives. The types of hydrocarbon derivatives depend entirely on the type of feedstock but do cause an increase in the heat content of the product gas.

In the oil gas method, an oil product (typically heavy fuel oil, as described above) is sprayed into the hot water gas chamber to produce a better quality (higher heat content) gas. The amount of the heavy fuel ratio is a determinant of the quality of the gas. In the 19th century and early 20th century, this was the method used to produce the town gas but has largely been superseded by natural gas in countries with an abundant supply. As supplies of natural gas diminish and various carbonaceous feedstocks are used for gas production, the process may once again rise in importance.

See also: Carbureted Blue Gas.

Catalysts

A catalyst is a chemical agent which, when added to a reaction (process), will enhance the conversion of a feedstock without being consumed in the process.

Catalysts are indispensable in the fuel production and refining and petrochemical industry for routine production of gasoline, diesel fuels, jet fuels, heavy oil hydrocarbon derivatives, petrochemicals, and plastics. Hydrocarbon derivatives (HT and HDS) and residue hydrodesulfurization (RDS) are the major processes for converting crude oil into these crude oil products.

During processing, catalysts will become contaminated with impurities in the crude oil feed and become deactivated. When that happens, they are usually sent for regeneration where contaminants are removed. Ultimately, they will be contaminated with coke, sulfur, vanadium, and nickel in a manner and at a level that makes regeneration impractical. At this stage, catalysts are considered *spent* and they may pose significant environmental problems, as landfill disposal is no longer accepted as best practice.

Hydrodesulfurization (HDS/RDS) of heavy oil produces spent catalysts that contain molybdenum (Mo), vanadium (V), nickel (Ni), or cobalt (Co) at concentration levels that have been found to be economical for recovery. Due to its complex nature, metal recovery from the spent catalysts from hydrodesulfurization processes involves a combination of pyro- and hydro-metallurgical processes. With increasing demand of ever more complex metallic

composite and alloy materials in modern manufacturing processes, it becomes imperative to develop appropriate methods for the recovery of these valuable metals.

See also: Refining.

Catalysts – Activity

The ratio of the space velocity of the catalyst under test to the space velocity required for the standard catalyst to give the same conversion as the catalyst being tested; usually multiplied by 100 before being reported.

A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. Catalysts that have the same phase as the reactants are homogeneous catalysts (e.g., enzymes in biochemical reactions or transition-metal complexes used in the liquid phase for catalyzing organic reactions). Those that have a different phase from the reactants are heterogeneous catalysts (e.g., metals or oxides used in many industrial gas reactions).

As a catalyst takes part in the chemical reaction, but is not consumed by the reaction, the catalyst must be a reactant in one of the first steps in the mechanism and a product in one of the last steps. The reaction proceeds in a cyclic fashion, where the catalyst, or more correctly the catalytic sites, are regenerated and used again and again. The catalyst provides an alternative pathway by which the reaction can proceed, in which the activation energy is lower. It thus increases the rate at which the reaction comes to equilibrium, although it does not alter the position of the equilibrium. The catalyst itself takes part in the reaction and consequently may undergo physical change (e.g., conversion into powder). In certain circumstances, small quantities of catalyst can speed up reactions. Most catalysts are also highly specific in the type of reaction they catalyze, particularly enzymes in biochemical reactions. Generally, the term is used for a substance that increases reaction rate (a positive catalyst). Some reactions can be slowed down by negative catalysts.

The increase in the rate of a specified chemical reaction caused by catalyst under specified conditions is called catalytic activity. Activity of a catalyst is a measure of the rate of conversion of the starting material by the catalyst. For homogeneous catalysts, activity is expressed as rate constant per mole of catalyst. For heterogeneous solid catalysts, the activity is generally expressed as reaction rate or the rate constant per unit mass, volume, or surface area of the catalyst. In general, the catalyst activity can be defined as the fractional conversion of starting material under standardized conditions.

The activity of a catalyst is determined by measuring the specific rate of the catalyzed reaction in which the desired product forms. The specific rate of the catalytic reaction is the rate increase caused by unit mass, volume, or surface area of catalyst compared to the rate of uncatalyzed reaction. This is usually represented by a power rate equation. For example, for a reaction $A + B \rightarrow C$, the reaction rate r is represented by the following equation:

$$r = k c_A^a c_B^b c_C^c$$

In this equation, k is the reaction rate constant; c_A , c_B , and c_C are the concentrations (partial pressures) of the reactants and product; and a , b , and c are the respective orders of reactions.

The reaction rate or the catalyst activity is dependent on the temperature. This relation is represented by the following equation:

$$r = A \exp (-E/RT)$$

where A is the pre-exponential factor and E is the apparent activation energy. From this equation, the catalyst activity is exponentially proportional to the temperature. Activity can generally be stepped up by raising the temperature, although frequent raising of the temperature can shorten the life of the catalyst or increases undesirable reactions that may be catalytic, thermal, or both. A higher temperature can also decrease the maximum conversion obtainable if the reaction is exothermic and is limited in extent by thermodynamic equilibrium.

Other factors being equal, the activity of a solid catalyst increases with its surface area exposed to the reactants. The activity of the exposed surface is generally not uniform throughout the available surface area. For example, the activity of a supported metal catalyst resides in the exposed metal atoms dispersed on the support, while the bare support is generally inactive. Because the number of exposed metal atoms per unit mass or unit volume of the catalyst can be determined by chemisorption measurement, catalytic activity can, in these cases, be defined in terms of the number of reactant molecules converted per exposed metal atom per second. This measure of activity is the turnover number or turnover frequency. This number essentially characterizes the rate of reaction per active site, and therefore the method used for determination of the number of exposed active atoms must be carefully selected and clearly specified. The activity of a catalyst can, then, be written as a product of two factors, the number of active sites, and the turnover frequency. For well-defined homogeneous catalytic reactions, the turnover number can be directly determined by calculating the number of molecules converted per second per catalyst molecule in solution.

Apart from activity, the usefulness of the catalyst also depends on its selectivity and stability. Selectivity is a measure of the relative rate of formation of each product from two or more competing reactions, and is usually expressed as a fraction or percentage of the total conversion. Of particular importance is the selectivity for the desired reaction product. A catalyst may be useful for its activity or its selectivity or both. If a variety of reactions are possible, then selectivity is more important. Stability of the catalyst toward chemical, thermal, or mechanical degradation or decomposition determines the useful life of the catalyst during which it maintains both its activity and selectivity at the fixed levels. Catalyst stability is also referred to as catalyst life, and a number of different processes can contribute to the loss of catalytic activity including coking, fouling, sintering, and poisoning. These catalyst deactivation processes are briefly discussed below.

Catalyst – Deactivation

Catalysts suffer a decline in activity with time-on-stream (*catalyst deactivation*). The time frame for this decline is large compared to the cycle of the transformation of a molecule of reactant to product, but brief in contrast to the natural enzyme. For example, the lifetime of a cracking catalyst is of the order of seconds while that of a reforming catalyst or that of the promoted catalyst in the synthesis of ammonia is measured in years.

Catalyst regeneration can restore catalyst activity. For example, coking catalysts can be restored by oxidation. However, other instances of catalyst deactivation such as sintering and/or irreversible phase transformation may be difficult to regenerate. In addition, catalyst deactivation by poisoning refers to the reversible/irreversible adsorption of small quantity of material on the active sites of the catalyst surface. The adsorbed material may be an impurity in the feed or an unwanted product of the reaction.

See also: Catalyst, Refining.

Catalyst Fouling

Fouling is a physical phenomenon in which coke or other inorganic foulants are deposited on the catalyst surface blocking the active sites and pores. The generic name coke indeed represents a variety of carbonaceous deposits widely varying in chemical nature. It varies from graphitic filamentous carbon to amorphous polymeric films. Coke formed from the gas phase reactions are more carbonaceous, while coke formed in liquid phase reactions may contain polycyclic aromatic molecules. Different types of cokes require different types of regeneration techniques and operating environments. Carbonaceous deposits can be removed by gasification using steam and air.

Coke is preferably gasified by reaction with oxygen as it is fast and efficient, but careful temperature control is needed to avoid the exothermic heat of reaction effecting thermal reorganization. To achieve temperature control, gasification by steam can be carried out with exothermic gasification by oxygen. Control can be achieved by conducting the gasification in two or more stages as is done in reforming catalysts. A mixture of steam and air is employed with a maximum of 2% air in the mixture. After gasification, nitrogen purging followed by reduction with hydrogen at 310°C (590°F) is carried out.

In the steam reforming process, the nickel catalyst supports both carbon formation and removal but potassium oxide (K_2O) or magnesium oxide (MgO , also called magnesia) is added to the catalyst only to increase the degree of coke gasification.

Inorganic foulants can be removed from catalyst by washing. A contamination from lubricating oil on emission control catalyst can result in phosphorus-glazed coatings. Such coatings must be removed by controlled dissolution and washing without seriously damaging the catalyst.

Methanation catalyst can sometimes be contaminated by carry-over from the carbon dioxide removal section. Although contaminants like potassium carbonate do not poison the catalyst, they physically block the catalyst surface and reduce the effectiveness. Such catalysts can be reactivated by back washing with clean condensate. While monoethanolamine and diethanolamine can also be washed off successfully, satisfactory reactivation of catalyst contaminated with sulfinol or vetrocoke solutions is difficult.

Solid acid catalysts for alkylation have recently received interest as an alternative to environmentally hazardous liquid phase catalysts such as sulfuric acid and hydrogen fluoride. The coke formed during the isobutane alkylation with C_4 olefins with Y zeolite catalysts is highly hydrogenated. Upon heating at low temperatures, this coke desorbs as hydrocarbon derivatives and simultaneously changes from an aliphatic structure to an aromatic one. This modification is the reason of the difficulty found in completely removing the coke from these types of catalysts. Combining an initial treatment in ozone followed by a treatment in hydrogen (H_2) or helium (He) helps the regeneration process.

Catalysts – Hydrogen Production

Hydrogen plants are one of the most extensive users of catalysts in the refinery. Catalytic operations – in which the catalyst is an important (necessary) aspect of the hydrogen production process – include (i) steam reforming, (ii) shift conversion, and (iii) methanation.

Reforming Catalysts

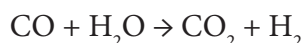
The reforming catalyst is usually supplied as nickel oxide that, during start-up, is heated in a stream of inert gas, then steam. When the catalyst is near the normal operating temperature, hydrogen or a light hydrocarbon is added to reduce the nickel oxide to metallic nickel. The high temperatures (up to 870°C , $1,600^\circ\text{F}$) and the nature of the reforming reaction require that the reforming catalyst be used inside the radiant tubes of a reforming furnace. The active agent in reforming catalyst is nickel, and normally, the reaction is controlled both by diffusion and by heat transfer. Catalyst life is limited as much by physical breakdown as by deactivation.

Sulfur is the main catalyst poison, and the catalyst poisoning is theoretically reversible with the catalyst being restored to near full activity by steaming. However, in practice, the deactivation may cause the catalyst to overheat and coke, to the point that it must be replaced. Reforming catalysts are also sensitive to poisoning by heavy metals, although these are rarely present in low-boiling hydrocarbon feedstocks and in naphtha feedstocks. Coke deposition on the reforming catalyst and ensuing gloss of catalyst activity are the most characteristic issues that must be assessed and mitigated.

A common steam-methane reforming catalyst uses nickel on an alpha-alumina ceramic carrier that is acidic in nature. Promotion of hydrocarbon cracking with such a catalyst leads to coke formation from higher boiling feedstocks. Some catalyst formulations use a magnesia/alumina (MgO/Al_2O_3) support that is less acidic than α -alumina that reduces cracking on the support and allows higher boiling feedstocks (such as liquefied petroleum gas) to be used.

Shift Conversion Catalysts

The second important reaction in a steam reforming plant is the shift conversion reaction:



Two basic types of shift catalyst are used in steam reforming plants: iron/chrome high-temperature shift catalysts, and copper/zinc low-temperature shift catalysts.

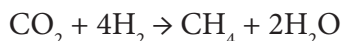
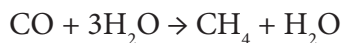
High-temperature shift catalysts operate in the range of 315 to 430°C (600 to 800°F) and consist primarily of magnetite (Fe_3O_4) with three-valent chromium oxide (Cr_2O_3) added as a stabilizer. The catalyst is usually supplied in the form of ferric oxide (Fe_2O_3) and six-valent chromium oxide (CrO_3) and is reduced by the hydrogen and carbon monoxide in the shift feed gas as part of the start-up procedure to produce the catalyst in the desired form. However, caution is necessary since if the steam/carbon ratio of the feedstock is too low and the reducing environment too strong, the catalyst can be reduced further, to metallic iron. Metallic iron is a catalyst for Fischer-Tropsch reactions, and hydrocarbons will be produced.

Low-temperature shift catalysts operate at temperatures on the order of 205 to 230°C (400 to 450°F). Because of the lower temperature, the reaction equilibrium is more controllable and lower amounts of carbon monoxide are produced. The low-temperature shift catalyst is primarily used in wet scrubbing plants that use a methanation for final purification. Pressure swing adsorption plants do not generally use a low-temperature since any unconverted carbon monoxide is recovered as reformer fuel. Low-temperature shift catalysts are sensitive to poisoning by sulfur and are sensitive to water (liquid) that can cause softening of the catalyst followed by crusting or plugging.

The catalyst is supplied as copper oxide (CuO) on a zinc oxide (ZnO) carrier, and the copper must be reduced by heating it in a stream of inert gas with measured quantities of hydrogen. The reduction of the copper oxide is strongly exothermic and must be closely monitored.

Methanation Catalysts

In wet scrubbing plants, the final hydrogen purification procedure is methanation in which the carbon monoxide and carbon dioxide are converted to methane:



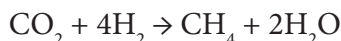
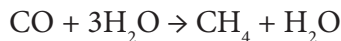
The active agent is nickel, on an alumina carrier.

The catalyst has a long life, as it operates under ideal conditions and is not exposed to poisons. The main source of deactivation is plugging from carry-over of carbon dioxide from removal solutions.

The most severe hazard arises from high levels of carbon monoxide or carbon dioxide that can result from breakdown of the carbon dioxide removal equipment or from exchanger tube leaks that quench the shift reaction. The results of breakthrough can be severe, since the methanation reaction produces a temperature rise of 70°C (125°F) per 1% of carbon monoxide or a temperature rise of 33°C (60°F) per 1% of carbon dioxide. While the normal operating temperature during methanation is approximately 315°C (600°F), it is possible to reach 700°C (1,300°F) in cases of major breakthrough.

Catalysts – Methanation

In wet scrubbing plants, the final hydrogen purification procedure is methanation in which the carbon monoxide and carbon dioxide are converted to methane:



The active agent is nickel, on an alumina carrier.

The catalyst has a long life, as it operates under ideal conditions and is not exposed to poisons. The main source of deactivation is plugging from carry-over of carbon dioxide from removal solutions.

The most severe hazard arises from high levels of carbon monoxide or carbon dioxide that can result from breakdown of the carbon dioxide removal equipment or from exchanger tube leaks that quench the shift reaction. The

results of breakthrough can be severe, since the methanation reaction produces a temperature rise of 70°C (125°F) per 1% of carbon monoxide or a temperature rise of 33°C (60°F) per 1% of carbon dioxide. While the normal operating temperature during methanation is approximately 315°C (600°F), it is possible to reach 700°C (1,300°F) in cases of major breakthrough.

Catalyst Poisoning

A catalyst poison is an impurity present in the feed stream that reduces catalyst activity. It adsorbs on active sites of the catalyst. This adsorption can be temporary or permanent depending on the strength of adsorption of the poison on the surface of the catalyst. In a multi-reaction environment, the poisoning may affect one reaction step more than another. In such cases, the selectivity toward a desired reaction may be improved by deliberate addition of a poison.

The strong interaction between some feed component and one or more of the products and the active sites of catalyst may change the nature of surface and catalytic activity leading to poisoning. Impurities such as organic bases for acidic catalysts or sulfur compounds over metal containing catalysts strongly chemisorb resulting in severe deactivation. A ppm level of sulfide in gas phase is sufficient to significantly cover the metal surface with sulfur. The first group of poisons involves Group VA and VIA elements, poison metal catalysts by interaction through their S and P orbitals. The strategy of changing the number of bonding electrons by oxidation or reduction can effectively reverse the poisoning. Thus, the poison efficiency of sulfur increases as $\text{SO}_4^{2-} < \text{SO}_2 < \text{H}_2\text{S}$. For hydrogenation of 2-butanone to 2-butanol at 373 K and 1.7 MPa, the complete activity recovery of Ni-supported catalyst with supercritical CO_2 extraction at 313 K and 41 MPa was found to be the best regeneration procedure. Sulfur poisoning of nickel catalysts is very frequent in industrial operations. The treatment for regeneration of a Ni/SiO₂ catalyst that was completely poisoned by thiophene during the benzene hydrogenation consisted of a sequence of oxidation-reduction treatments using low oxygen partial pressure mixtures and pure hydrogen, with intermediate argon stream purging at the same treatment temperature. This method is easy to carry out and quickly recovers up to 90% w/w of the sulfur.

The second group of poisons involves toxic heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd), and copper (Cu) that may form alloys with the catalyst. These poisons can be removed by abrasion or leaching. The third group of poisons is highly specific in strongly chemisorbing to a catalyst surface. Thus, for example, carbon monoxide poisons iron, but has negligible effect on copper or silver catalysts.

When high temperature shift catalysts are used with cyclic reformers, they get sulfided and contaminated with gums and carbon formed in the up-stream plant. Normally, the catalysts are regenerated by treatment with steam and air. Low temperature shift catalysts are more difficult to regenerate. The catalyst is first re-oxidized for removal of the sulfur poison, which is further washed with condensate to remove water-soluble poisons such as sulfate and chlorides. The treated catalyst is finally re-reduced.

Catalyst Regeneration

Most chemical processes use catalyst(s) as an aid to transform raw materials into finished products. The life of a catalyst varies from a fraction of a few seconds to several years depending on the severity and type of processes involved. All the catalysts used in chemical industries therefore come for regeneration at some time or the other. Alternatively, the catalysts have to be treated for recovery of their contents before being discarded for landfill operation. The decision of regeneration for catalysts is economical in nature and involves a trade-off between cost of regeneration and stringent requirement of environmental regulations.

Catalyst regeneration can be carried out in-situ within the same reactor at the site. Current environmental legislation and waste handling problems are, however, sufficiently discouraging that most companies favor ex-situ or off site regeneration. Carbonaceous and sulfur-containing deposits on the catalyst surface and pores are eliminated during the regeneration process and brought down to levels below 1 to 2% with 90-95% restoration of catalytic activity. Typically, parameters such as the crush strength, particle size, and size distribution, surface area, and metal contamination levels are used to assess the regenerability of the catalyst.

Efforts to develop new catalysts that last longer form the focus of current research in this area. The primary goal of this research is to create new designs to minimize deactivation and evolve proprietary chemical treatments to handle specific contaminants. Hybrid strategies involving thermal, mechanical, and chemical techniques are increasingly looked at to combat the menace. Improvements in regenerator efficiency – primarily through better temperature control and avoidance of physical damage to material (such as length-to-diameter ratio, uneven surface temperatures leading to sintering, etc.) are especially relevant to commercial practice.

Catalyst regeneration is an economically attractive option that also avoids the environmental legislation on waste disposal. Catalyst manufacturers and regenerator service providers are working together to devise new schemes to restore complete activity for reuse or secondary use of catalysts. Precise control on particle temperature and avoiding damage to catalyst hold the key for successful regeneration.

Catalysts – Selectivity and Conversion

Catalysts are highly specific compounds and have an ability to direct the reaction to yield a particular product. The ability of the catalyst to increase the rate of a particular reaction and chemisorption is the main factor in deciding the activity of a catalyst. The ability of the catalyst to direct a reaction to yield a particular product is referred to as the selectivity of the catalyst.

The reaction with same reactants but different catalyst may yield different products, which is termed as the selectivity of the catalyst, the relative activity of a catalyst with respect to a particular compound in a mixture, or the relative rate in competing reactions of a single reactant. Another term – conversion – refers to the disappearance of reactants during reaction.

See also: Adsorption, Chemisorption.

Catalyst Sintering

Overheating of catalysts leads to thermal degradation and loss of surface area resulting in decreasing catalyst activity. Sintering is normally difficult to reverse, and preventive methods are more useful than finding ways for remedies. Thus, for instance, carbon deposition and metal sintering are the major causes of deactivation of a naphtha catalytic reforming catalyst. During reforming, platinum crystallites range in size from 5 to 20 nanometers (5 to 230 nm). It is possible to redisperse the platinum by oxychlorination treatment using oxygen, a small amount of carbon tetrachloride (CCl_4), or hydrogen chloride (HCl) at 500°C (930°F). A platinum-iridium (Pt-Ir) bimetallic catalyst has also been treated in similar fashion but requires a higher treatment temperature of 550°C ($1,020^\circ\text{F}$).

The catalytic reaction takes place at the surface of the catalyst. For this reason, the catalyst must have a large area and the active component is present in the catalyst in the form of small particles, which are much less stable than large particles. A catalyst will slowly lose catalytic activity due to growth of the particle and loss of surface area.

There are two distinct mechanisms for sintering: (i) the crystallites may continuously emit and collect atoms; since the atoms will be more stable at the surface of a large particle than at the surface of a small particle, the atoms will on average migrate from the small particles to the large, or (ii) the particles may move, and when two particles come into contact, they may merge into a single, larger particle; the loss of catalytic activity due to particle growth is irreversible.

Catalysts – Solid Acid

Solid acid catalysts are environmentally friendly and highly versatile for reaction in aqueous, polar and non-polar medium as well as in gas phase. These catalysts offer non-corrosive atmosphere. A variety of industrially important reactions based on alkylation, etherification, esterification, hydrolysis, oligomerization, etc., can be carried out with these catalysts. Often, the rate and selectivity with solid acids are superior to that realized with homogeneous catalysts and, in many cases, reactions that are not feasible with homogeneous catalysts occur with solid acids. Solid acids

can be used in catalytic distillation columns and in extractive reaction modes and thus offer a number of advantages associated with capital and energy cost. Solid acids have been used for separation of close boiling isomeric/non-isomeric substances. These catalysts are used in oil refining and chemical industries. The development of new alkylation and isomerization processes using solid acids replacing liquid acids such as HF and H_2SO_4 is in progress for environmental as well as safety consideration.

Since the discovery of its strong acidity, sulfated zirconia and other sulfated metal oxides have attracted much attention as potential hydrocarbon process catalysts. These materials exhibit high acid strengths, in Hammet scale (H_0), of up to $\text{H}_0 \leq -16$. Numerous studies have been conducted on preparation, characterization, and catalytic activities of sulfated metal oxides. The usual practice of synthesis is the preparation of the hydroxide, which is then impregnated with sulfate using various precursors such as sulfuric acid (H_2SO_4), ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and sulfur trioxide (SO_3).

Heteropoly solid acids involve a large class of compounds, formed by the condensation of two or more different types of oxo-anions, containing a central atom, typically Si or P, tetrahedrally coordinated to oxygen and surrounded by oxygen-linked hexavalent 2 peripheral metal atoms.

X-ray diffraction (XRD) is used to measure the crystalline phases of the solid acids. The crystallinity of solid acids, particularly in sulfated zirconia, is an important physical property for them to be catalytically active. For instance, 600°C calcined zirconia is completely monoclinic whereas sulfated zirconia is completely tetragonal.

Due to the charge imbalance between Si^{4+} and Al^{3+} , zeolites are associated with metal ions or protons for the charge compensation. The chemical structure of bridged hydroxyls are proposed as a Si-OH group strongly influenced by a tricoordinated neighboring aluminum (Al^{3+}) atom.

The acidity in heteropolyacids is due to protons compensating the anions. In solid state, the protons are involved in formation of crystal structure of the heteropoly acids and in the protonation of more accessible terminal oxygen leading to the H_5O_2^+ species which link four neighboring heteropoly anions by forming hydrogen bonds with terminal $\text{W}=\text{O}$ oxygen. The states of protons were studied by high resolution solid state ^1H NMR. In the case of bulk hydrated heteropoly anions, it is observed by ^{17}O NMR of solid molybdophosphate that the terminal oxygens are predominant protonation sites. Heteropoly acids such as $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ have a relatively large number of strong Brønsted acid sites.

Catalyst Stripping

Catalyst stripping is the introduction of steam, at a point where spent catalyst leaves the reactor, in order to strip, i.e., remove, deposits retained on the catalyst.

An efficient catalyst stripper design is one that maximizes mass transfer between the two phases (the stripping steam flowing up and the fluidized catalyst flowing down the stripper vessel). Hydrocarbon derivatives in the catalyst phase need to be replaced with steam. To enhance this mass transfer phenomenon, the stripper internals should have the following characteristics: (i) maximum surface area for mass transfer per unit volume of the stripper vessel, (ii) maximum cross-sectional area of the vessel available for catalyst and steam to flow through, (iii) maximum active volume, such that there are stagnation or dead zones, (iv) uniform distribution of catalyst and steam to avoid channeling and by-passing, (v) increased contact time and mixing between the two phases, (vi) excellent fluidization quality, (vii) plug flow conditions, and (viii) mechanically robust to withstand service.

Catalytic Cracking

The conversion of high-boiling feedstocks into lower boiling products by means of a catalyst which may be used in a fixed bed or fluid bed.

Catalytic cracking is basically the same as thermal cracking, but it differs by the use of a catalyst that is not consumed in the process and it is one of several practical applications used in a refinery that employ a catalyst to improve process efficiency. The original incentive to develop cracking processes arose from the need to increase gasoline supplies and to increase the octane number of gasoline, while maintaining yield from high-boiling stocks

using catalysts. Since cracking could virtually double the volume of gasoline from a barrel of crude oil, the purpose of cracking was wholly justified.

Most catalysts used in catalytic cracking consist of mixtures of crystalline synthetic silica-alumina, termed *zeolites*, and amorphous synthetic silica-alumina. The catalytic cracking processes, as well as most other refinery catalytic processes, produce coke which collects on the catalyst surface and diminishes its catalytic properties. The catalyst, therefore, needs to be regenerated continuously or periodically essentially by burning the coke off the catalyst at high temperatures. The method and frequency in which catalysts are regenerated are a major factor in the design of catalytic cracking units. A number of different catalytic cracking designs are currently in use in the United States, including fixed-bed reactors, moving-bed reactors, fluidized-bed reactors, and once-through units. The fluidized- and moving-bed reactors are by far the most prevalent.

An important purpose evolved from the ability of cracked gasoline to resist detonation that is the cause of knocking in automobile engines. In the early days of automobile engine development, *straight-run gasoline* had a lower end point (165°C, 330°F) than that of *cracked gasoline* (205°C, 400°F) and, furthermore, did not color when exposed to sunlight. Similar exposure caused the cracked gasoline to turn brown, and hence straight-run gasoline was regarded as the premium material.

Gasoline is now produced, for the most part, by catalytic cracking processes or by reforming processes. In catalytic cracking, the crude oil (or crude oil-derived feedstock) is fed into a reaction vessel containing a catalyst. In reforming processes, naphtha (refined or unrefined) that may have been produced by catalytic cracking of higher molecular weight feedstocks, is heated with hydrogen in the presence of a catalyst. Reforming causes a rearrangement of the structures of the molecular constituents and creates a gasoline product.

Catalytic cracking has a number of advantages over thermal cracking. Gasoline produced by catalytic cracking has a higher octane number and consists largely of *iso*-paraffins and aromatics. The *iso*-paraffins and aromatic hydrocarbon derivatives have high octane numbers and greater chemical stability than mono-olefins ($R-CH=CH_2$ or $R-CH=CH-R^1$) and diolefins ($R-CH=CH-CH=CH_2$ or $R-CH=CH(CH_2)_nCH=CH-R^1$). The olefins and diolefins are present in much greater quantities in gasoline produced by thermal cracking processes. Furthermore, substantial quantities of olefin gases and smaller quantities of methane (CH_4), ethane (CH_3CH_3), and ethylene ($CH_2=CH_2$) are produced by catalytic cracking. The olefin gases are suitable for polymer gasoline manufacture.

Sulfur compounds are changed in such a way that the sulfur content of gasoline produced by catalytic cracking gasoline is lower than the sulfur content of gasoline produced by thermal cracking. Catalytic cracking produces less residuum and more of the useful gas oil constituents than thermal cracking. Finally, the process has considerable flexibility, permitting the manufacture of both motor gasoline and aviation gasoline and a variation in the gas oil production to meet changes in the fuel oil market.

The feedstocks for catalytic cracking can be any one (or blends) of the following: (i) straight-run gas oil, (ii) vacuum gas oil, (iii) atmospheric residuum, and (iv) vacuum residuum. If blends of the above feedstocks are employed, compatibility of the constituents of the blends must be assured under read to conditions or excessive coke will be laid down on to the catalyst. In addition, there are several pretreatment options for the feedstocks for catalytic cracking units and these are (i) deasphalting to prevent excessive coking on catalyst surfaces, (ii) demetallation, i.e., removal of nickel, vanadium, and iron to prevent catalyst deactivation, (iii) use of a short residence time as a means of preparing the feedstock, and (iv) hydrotreating or mild hydrocracking to prevent excessive coking in the fluid catalytic cracking unit.

In addition, the goal is to reduce the sulfur content of the naphtha and there is a number of process options for reducing the sulfur level in fluid catalytic cracker naphtha; the two options that are generating the most interest are (i) hydrotreat the feedstock to the catalytic cracking unit; and (ii) hydrotreat the naphtha from the catalytic cracker.

Hydrotreating the fluid catalytic cracker feed improves naphtha yield and quality and reduces the sulfur oxide (SO_x) emissions from the catalytic cracker unit, but it is typically a high-pressure process and, furthermore, manipulation of feedstock sulfur alone may not be sufficient to meet future gasoline performance standards. Refineries wishing to process heavier crude oil may only have the option to desulfurize the resulting higher-sulfur naphtha. Hydrodesulfurization of catalytic cracker naphtha is a low-pressure process. Obviously, the selection of an optimum hydrotreating process option for reducing sulfur in catalytic cracker naphtha is determined by economic factors specific to a refinery and to the feedstock. Hydrotreating catalytic cracker feedstock can be very profitable for a refiner despite its large capital investment. By taking advantage of feedstock hydrotreating, margins can be optimized by considering the feedstock hydrotreater unit, the fluid catalytic cracker, and any post-catalytic cracker hydrotreater as one integrated upgrading step.

Catalytic cracking in the usual commercial process involves contacting a feedstock (usually a gas oil fraction) with a catalyst under suitable conditions of temperature, pressure, and residence time. By this means, a substantial part (>50%) of the feedstock is converted into gasoline and lower boiling products, usually in a single-pass operation. However, during the cracking reaction, carbonaceous material is deposited on the catalyst, which markedly reduces its activity, and removal of the deposit is very necessary. The carbonaceous deposit arises from the thermal decomposition of high molecular weight polar species in the feedstock. Removal of the deposit from the catalyst is usually accomplished by burning in the presence of air until catalyst activity is reestablished.

The reactions that occur during catalytic cracking are complex, but there is a measure of predictability now that catalyst activity is better understood. The major catalytic cracking reaction exhibited by paraffins is carbon-carbon bond scission into a lower-boiling paraffin derivative and an olefin. Bond rupture occurs at certain definite locations on the paraffin molecule, rather than randomly as in thermal cracking. For example, paraffins tend to crack toward the center of the molecule, the long chains cracking in several places simultaneously. Normal paraffins usually crack at carbon-carbon bonds or still nearer the center of the molecule. On the other hand, iso-paraffins tend to rupture between carbon atoms that are adjacent to a tertiary carbon atom. In either case, catalytic cracking tends to yield products containing three or four carbon atoms rather than the one- or two-carbon atom molecules produced in thermal cracking.

As in thermal cracking, high molecular weight species usually crack more readily than small molecules. However, paraffins having more than six carbon atoms may also undergo rearrangement of their carbon skeletons before cracking, and a minor amount of *dehydrocyclization* also occurs, yielding aromatics and hydrogen.

Olefins are the most reactive class of hydrocarbon derivatives in catalytic cracking and tend to crack from 1,000 to 10,000 times faster than in thermal processes. Severe cracking conditions destroy olefins almost completely, except for those in the low-boiling gasoline and gaseous hydrocarbon range and, as in the catalytic cracking of paraffins, *iso*-olefins crack more readily than *n*-olefins.

Olefins also tend to undergo rapid *isomerization* and yield mixtures with an equilibrium distribution of double-bond positions. In addition, the chain-branching isomerization of olefins is fairly rapid and often reaches equilibrium. These branched-chain olefins can then undergo *hydrogen transfer* reactions with naphthenes and other hydrocarbon derivatives. Other olefin reactions include *polymerization* as well as *condensation* to yield aromatic molecules, which in turn may be the precursors of coke formation.

Cycloparaffins (naphthenes) catalytically crack more readily than paraffins but not as readily as olefins. Naphthene cracking occurs by both ring and chain rupture and yields olefins and paraffins, but formation of methane and the C_2 hydrocarbon derivatives (ethane, CH_3CH_3 , ethylene, $CH_2=CH_2$, and acetylene, $CH\equiv CH$) is relatively minor if present at all.

Aromatic hydrocarbon derivatives exhibit wide variations in their susceptibility to catalytic cracking. The benzene ring is relatively inert, and condensed-ring compounds, such as naphthalene, anthracene, and phenanthrene, crack very slowly. When these aromatics crack, a substantial part of their *conversion* is reflected in the amount of coke deposited on the catalyst. Alkylbenzenes with attached groups of C_2 or larger primarily form benzene and the corresponding olefins, and heat sensitivity increases as the size of the alkyl group increases.

Catalytic Cracking Chemistry

Catalytic cracking is the thermal decomposition of crude oil constituents hydrocarbon derivatives in the presence of a catalyst.

Clay minerals form a family of crystalline aluminosilicate solids, and the acid treatment develops acidic sites by removing aluminum from the structure. The acid sites also catalyze the formation of coke, and Houdry developed a moving bed process that continuously removed the cooked beads from the reactor for regeneration by oxidation with air.

Although thermal cracking is a free radical (neutral) process, catalytic cracking is an ionic process involving carbonium ions, which are hydrocarbon ions having a positive charge on a carbon atom. The formation of carbonium ions during catalytic cracking can occur by: (i) addition of a proton from an acid catalyst to an olefin, and/or (ii) abstraction of a hydride ion (H^-) from a hydrocarbon by the acid catalyst or by another carbonium ion.

However, carbonium ions are not formed by cleavage of a carbon-carbon bond. In essence, the use of a catalyst permits alternate routes for cracking reactions, usually by lowering the free energy of activation for the reaction. The acid catalysts first used in catalytic cracking were amorphous solids composed of approximately 87% silica (SiO_2) and 13% alumina (Al_2O_3) and were designated low-alumina catalysts. However, this type of catalyst is now being replaced by crystalline aluminosilicates (zeolites) or molecular sieves.

The first catalysts used for catalytic cracking were acid-treated clays, formed into beads. In fact, clays are still employed as catalyst in some cracking processes.

Like the paraffins, naphthenes do not appear to isomerize before cracking. However, the naphthenic hydrocarbon derivatives (from C_9 upward) produce considerable amounts of aromatic hydrocarbon derivatives during catalytic cracking. Reaction schemes similar to that outlined here provide possible routes for the conversion of naphthenes to aromatics. Alkylated benzenes undergo nearly quantitative dealkylation to benzene without apparent ring degradation below 500°C (930°F). However, polymethyl benzene derivatives undergo disproportionation and isomerization with little benzene formation.

Coke formation is considered, with just cause to a malignant side reaction of normal carbenium ions. However, while chain reactions dominate events occurring on the surface, and produce the majority of products, certain less desirable bimolecular events have a finite chance of involving the same carbenium ions in a bimolecular interaction with one another. Of these reactions, most will produce a paraffin and leave carbene/carboid-type species on the surface. This carbene/carboid-type species can produce other products, but the most damaging product will be one which remains on the catalyst surface and cannot be desorbed and results in the formation of coke, or remains in a non-coke form but effectively blocks the active sites of the catalyst.

A general reaction sequence for coke formation from paraffins involves oligomerization, cyclization, and dehydrogenation of small molecules at active sites within zeolite pores:

Alkanes $\rightarrow$ alkenes

Alkenes $\rightarrow$ oligomers

Oligomers $\rightarrow$ naphthenes

Naphthenes $\rightarrow$ aromatics

Aromatics $\rightarrow$ coke

Whether or not these are the true steps to coke formation can only be surmised. The problem with this reaction sequence is that it ignores sequential reactions in favor of consecutive reactions. And it must be accepted that the chemistry leading up to coke formation is a complex process, consisting of many sequential and parallel reactions.

Catalytic Cracking Processes

Catalytic cracking is another innovation that truly belongs to the 20th century. It is the modern method for converting high-boiling crude oil fractions, such as gas oil, into gasoline and other low-boiling fractions. The several processes currently employed in catalytic cracking differ mainly in the method of catalyst handling, although there is an overlap with regard to catalyst type and the nature of the products. The catalyst, which may be an activated natural or synthetic material, is employed in bead, pellet, or microspherical form and can be used as a *fixed bed*, *moving-bed*, or *fluid-bed* configurations.

The fixed-bed process was the first to be used commercially and uses a static bed of catalyst in several reactors, which allows a continuous flow of feedstock to be maintained. Thus, the cycle of operations consists of (i) flow of feedstock through the catalyst bed, (ii) discontinuance of feedstock flow and removal of coke from the catalyst by burning, and (iii) insertion of the reactor on-stream.

The moving-bed process uses a reaction vessel in which cracking takes place and a kiln in which the spent catalyst is regenerated; catalyst movement between the vessels is provided by various means.

The fluid-bed process differs from the fixed-bed and moving-bed processes insofar as the powdered catalyst is circulated essentially as a fluid with the feedstock. The several fluid catalytic cracking processes in use differ primarily in mechanical design. Side-by-side, reactor-regenerator configuration or the reactor either above or below the regenerator is the main mechanical variation. From a flow standpoint, all fluid catalytic cracking processes contact the feedstock and any recycle streams with the finely divided catalyst in the reactor.

Feedstocks may range from naphtha to atmospheric residuum (*reduced crude*). Feed preparation (to remove *metallic constituents* and *high-molecular-weight non-volatile materials*) is usually carried out through any one of the following ways: coking, propane deasphalting, furfural extraction, vacuum distillation, viscosity breaking, thermal cracking, and hydrosulfurization.

The major process variables are temperature, pressure, catalyst-feedstock ratio (ratio of the weight of catalyst entering the reactor per hour to the weight of feedstock charged per hour), and space velocity (weight or volume of the feedstock charged per hour per weight or volume of catalyst in the reaction zone). Increased conversion can be obtained by applying higher temperature or higher pressure. Alternatively, lower space velocity and higher catalyst-feedstock ratio will also contribute to an increased conversion.

When cracking is conducted in a single stage, the more reactive hydrocarbon derivatives may be cracked, with a high conversion to gas and coke, in the reaction time necessary for reasonable conversion of the more refractory hydrocarbon derivatives. However, in a two-stage process, gas and gasoline from a short-reaction-time, high-temperature cracking operation is separated before the main cracking reactions take place in a second-stage reactor.

Catalytic Cracking – Process Parameters

The three main components of a fluid catalytic cracking unit are: (i) the reactor, (ii) the stripper, and (iii) the regenerator.

In the unit, the catalyst and the feed and product hydrocarbon derivatives are lifted up the riser pipe to the *reactor* where the predominately endothermic cracking processes take place. Since the reactions are endothermic, reaction temperature declines from bottom to top. At the top, the mixture enters a solid-gas separator, and the product vapors are led away. Cracked gases are separated and fractionated; the catalyst and residue, together with recycle oil from a second-stage fractionator, pass to the main reactor for further cracking. The products of this second-stage reaction are gas, gasoline, and gas oil streams, and recycle oil.

The coked catalyst enters the *stripper* where steam is added and unreacted-reacted hydrocarbon derivatives adsorbed on the catalyst are released. The stripped catalyst is then directed into the regenerator where air is added and the combustion of coke on the catalyst (and any hydrocarbon derivatives still adsorbed which were not stripped) occurs with the liberation of heat. Regenerator temperatures are typically 705 to 760°C (1300 to 1,400°F). Heat exchangers and the circulating catalyst capture the heat evolved during regeneration to be used in pre-heating the reactor feed to appropriate cracking temperatures (usually in the range, 495 to 550°C (925 to 1,020°F).

During operations, the entire catalyst inventory is *continually* circulated through the unit. Catalyst residence time in the riser reactor section is typically 1 to 3 seconds (with current trends to even shorter residence times), and the entire reactor-stripper-regenerator cycle is less than 10 minutes. To achieve cycle times of this order, catalyst circulation rates as high as 1 ton per second in large units are required. To withstand such movement, the catalyst must be sufficiently *robust* to withstand the operational stress.

Process temperatures are high, coke is repeatedly deposited and burned off, and the catalyst particles are moving at high speed through steel reactors and pipes. Contact between the catalyst particles and the metal walls and inter-particle contact are unavoidable. Thus, catalyst loss from the unit caused by poor attrition resistance can be a serious problem, since the quantities lost must be replaced by fresh catalyst additions to maintain constant unit performance. Catalyst manufacturers work hard to prevent inordinate losses due to attrition, and refineries keep a close watch on catalyst quality to be sure the produce conforms to their specifications. Therefore, the robustness of the catalyst is carefully monitored and controlled to a high attrition resistance that is determined by rigorous test methods that place a semi-quantitative evaluation on attrition resistance, which is generally related to breakdown with time in commercial units.

As intimated above, in some units, cracking does not always take place in the reactor and reaction often occurs in the vertical or upward sloped pipe called the *riser* (giving credence to the name *riser reactor* and *riser pipe cracking*) forming products, including coke. Pre-heated feedstock is sprayed into the base of the riser via feed nozzles where it contacts extremely hot fluidized catalyst at 1,230 to 1,400°F (665 to 760°C). The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high molecular weight oil into lower-boiling components including liquefied petroleum oil gas, constituents, gasoline, and diesel fuel. The catalyst-hydrocarbon mixture flows upward through the riser for just a few seconds, and then the mixture is separated via cyclones. The catalyst-free hydrocarbon derivatives are routed to a main fractionator for separation into fuel gas, propane and butanes, gasoline, low-boiling low density cycle oils used in diesel fuel and jet fuel, and heavy fuel oil.

The primary variables available to the operation of fluid catalytic cracking units for maximum unit conversion for a given feedstock quality include catalytic variables such as: (i) catalyst activity and (ii) catalyst design, which includes availability of cracking sites and the presence of carbon on the regenerated catalyst.

The equilibrium catalyst activity, as measured by a microactivity test (MAT), is a measure of the availability of zeolite and active matrix cracking sites for conversion. Therefore, an increase in the unit activity can effect an increase in conversion, and activity is increased by one, or a combination of (i) increased fresh catalyst addition rate, (ii) increased fresh catalyst zeolite activity, (iii) increased fresh catalyst matrix activity, (iv) addition of catalyst additives to trap or passivate the deleterious effects of feed nitrogen, alkalis (i.e., calcium and sodium), vanadium, and other feed metal contaminants, and (v) increased fresh catalyst matrix surface area to trap or remove feedstock contaminants.

In general, a two-digit increase in the activity as determined by the microactivity test activity appears to coincide with a 1% absolute increase in conversion. The increased matrix surface area improves conversion by providing more amorphous sites for cracking high boiling range compounds in the feedstock which cannot be cracked by the zeolite. Increased zeolite, on the other hand, provides the necessary acid cracking sites for selectively decomposing the amorphous cracked high boiling compounds and lower-boiling products.

In addition to zeolite and matrix activity, many of the physical and chemical properties of the catalyst (i.e., catalyst design) contribute to increased conversion through selectivity differences. These include zeolite type, pore size distribution, relative matrix to total surface area, and chemical composition.

Increasing the concentration of catalyst in the reactor, often referred to as cat/oil ratio, will increase the availability of cracking for maximum conversion, assuming the unit is not already operating at a catalyst circulation limit. This can be achieved by increasing reactor heat load or switching to a lower coke selective (i.e., lower delta coke) catalyst. Reactor heat load can be raised by increased reactor temperature or lower feed preheat temperature. This, in turn, increases the cat/oil ratio to maintain the unit in heat balance.

The lower the *carbon on regenerated catalyst*, the higher the availability of cracking sites since less coke is blocking acid cracking sites. The carbon on the regenerated catalyst is reduced by increasing regeneration efficiency through the use of carbon monoxide oxidation promoters. Carbon on the regenerated catalyst can also be reduced by more efficient air and spent catalyst contact. Increased regenerator bed levels also reduce the amount of carbon on the regenerated catalyst through increased residence time, but this must be traded off with reduced dilute phase disengager residence time and the possibility for increased catalyst losses.

There are also process variables that include (i) pressure, (ii) reaction time, and (iii) reactor temperature. Higher conversion and coke yield are thermodynamically favored by higher *pressure*. However, pressure is usually varied over a very narrow range due to limited air blower horsepower. Conversion is not significantly affected by unit pressure since a substantial increase in pressure is required to significantly increase conversion.

An increase in *reaction time* available for cracking also increases conversion. Fresh feed rate, riser steam rate, recycle rate, and pressure are the primary operating variables which affect reaction time for a given unit configuration. Conversion varies inversely with these stream rates due to limited reactor size available for cracking. Conversion has been increased by a decrease in rate in injection of fresh feedstock. Under these circumstances, over-cracking of gasoline to liquefied crude oil gas and to and dry gas may occur due to the increase in reactor residence time. One approach to offset any potential gasoline over-cracking is to add additional riser steam to lower hydrocarbon partial pressure for more selective cracking. Alternatively, an operator may choose to lower reactor pressure or increase the recycle rate to decrease residence time. Gasoline over-cracking may be controlled by reducing the availability of catalytic cracking sites by lowering cat/oil ratio.

Increased *reactor temperature* increases feedstock conversion, primarily through a higher rate of reaction for the endothermic cracking reaction and also through increased cat/oil ratio. A 5.5°C (10°F) increase in reactor

temperature can increase conversion by 1 to 2% absolute, but, again, this is feedstock dependent. Higher reactor temperature also increases the amount of olefins in gasoline and in the gases. This is due to the higher rate of primary cracking reactions relative to secondary hydrogen transfer reactions which saturate olefins in the gasoline boiling range and lower gasoline octane.

However, these variables are not always available for maximizing conversion since most fluid catalytic cracking units operate at an optimum conversion level corresponding to a given feed rate, feed quality, set of processing objectives, and catalyst at one or more unit constraints (e.g., wet gas compressor capacity, fractionation capacity, air blower capacity, reactor temperature, regenerator temperature, catalyst circulation). Once the optimum conversion level is found, there are very few additional degrees of freedom for changing the operating variables.

Catalytic Gas Conversion Process

The catalytic conversion of hydrogen cyanide (HCN) and carbonyl sulfide (COS) is a process used to mitigate the harmful effects of these components in gas streams by hydrolysis. Hydrolysis technology has two main fields of application, and these are (i) synthesis gas treatment upstream of an amine unit for coal or oil gasification processes, and (ii) other synthesis gas treatment where the presence of hydrogen cyanide and/or carbonyl sulfide is not acceptable to downstream processing units.

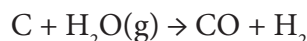
See also: Gas Cleaning, Gas Processing, Gas Treating.

Catalytic Gasification

The concept of hydrogasification, while superficially seeming to effectively yield a gas ideal for the production of synthetic natural gas, in fact departs considerably from the idealized gasification reaction.

The ideal gasification reaction is essentially thermally neutral, so temperature control is not a problem. Further, the supply of a separate oxidant is not required, so the cost of producing pure oxygen or separating nitrogen from the off gas is avoided. Steam is the only gasification agent used, and downstream gas shift and methanation steps are eliminated.

By contrast, hydrogasification requires a hydrogen supply which is normally produced by the highly endothermic high temperature carbon-steam reaction.



Pure oxygen must be supplied to provide the heat of reaction by combustion with some of the coal. In addition, a gas shift step is required to convert the carbon monoxide to additional hydrogen, and the carbon dioxide produced is normally removed upstream of the hydrogasification unit.

The relatively pure hydrogen stream is then reacted with carbon at low-to-moderate temperatures according to the carbon-hydrogen reaction. Because this reaction is highly exothermic, some means of temperature control is required. In addition, the previously discussed problems of coal agglomeration in hydrogen atmospheres have to be countered. Consequently, both the hydrogasifier itself and the hydrogasification process in general are more complex than, say, steam/oxygen gasification followed by shift and methanation.

The integration of the hydrogen production step into the Hygas gasifier does simplify the overall process, but has resulted in a very tall and complex gasifier. In addition, the gas produced by the Hygas process is not that much better for SNG production than the off gas from the established Lurgi gasifier.

The major problem with the ideal gasification route is that the rate of methane formation at low temperatures is slow relative to other gasification reactions. At higher temperatures, methane formation is not favored thermodynamically. One means of enhancing the rate of a specific reaction is by use of catalysts. It has been known for some time that alkali metals catalyze the reaction of carbon with steam to form mainly carbon monoxide and hydrogen. Potassium catalysts promote the gas phase shift and methanation reactions. This means that the products of carbon/steam gasification, essentially carbon monoxide and hydrogen, can be converted to methane within the gasifier. A further important advantage of alkali metal catalysts is that they reduce agglomeration of caking coals.

Earlier catalyst tests showed that the potassium must be available for combination with coal acids to be effective. Potassium hydroxide (KOH), potassium carbonate (K_2CO_3), and potassium sulfide (K_2S) are suitable catalysts, whereas the salts of strong acids such as potassium chloride (KCl) and potassium sulfate (K_2SO_4) do not have an affinity for the coal and are ineffective. It was further found that concentrations of potassium carbonate of from 10 to 20% w/w of the coal result in commercially acceptable gasification rates at 700°C (1290°F), in comparison to approximately 925°C (1,695°F) without catalyst.

While catalytic methane production at low temperature is significantly greater than that obtained with conventional gasifiers, the off gas still contains significant amounts of carbon monoxide, carbon dioxide, and hydrogen, in addition to steam. As in the conventional production of pipeline gas, these substances have to be removed or converted to methane. Instead of using a gas shift and a methanation step, in catalytic gasification, the carbon monoxide and hydrogen are separated and recycled to the gasifier. This is feasible, since the methanation reaction is close to equilibrium and there is consequently no buildup of hydrogen and carbon monoxide as would occur in an uncatalyzed system.

The addition of modest quantities of certain inorganic salts, such as alkali metal salts (such as potassium carbonate, sodium carbonate, potassium sulfide, sodium sulfide, and the like) will catalyze the steam gasification of coal. Potassium carbonate also acts as a catalyst for the methanation reaction.

In this process, crushed (-8 mesh) coal is treated with an aqueous solution of the catalyst after which the feed is dried and charged (through a system of lock hoppers) to the fluidized bed gasifier at 700°C (1,300°F) and 500 psi. The bed is fluidized by a mixture of steam and recycled carbon monoxide-hydrogen. Unreacted steam is condensed, and the acid gases (CO_2 , H_2S) are removed by conventional acid gas treatment. The product (methane) is separated from the carbon monoxide and hydrogen by a cryogenic process. The solid product (which is actually a mixture of char, coal minerals, and the catalyst) is removed on a continuous basis; the majority of the catalyst is recovered and recycled.

See also: Gasification, Gasification of Biomass.

Catalytic Oxidation Processes

Catalytic oxidation is a chemical conversion process that is used predominantly for destruction of volatile organic compounds and carbon monoxide. The process is used predominantly for destruction of volatile organic compounds and carbon monoxide. These systems operate in a temperature regime of 205 to 595°C (400 to 1,100°F) in the presence of a catalyst. Without the catalyst, the system would require higher temperatures. Typically, the catalysts used are a combination of noble metals deposited on a ceramic base in a variety of configurations (e.g., honeycomb-shaped) to enhance good surface contact.

Catalytic systems are usually classified on the basis of bed types such as fixed bed (or packed bed) and fluid bed (fluidized bed). These systems generally have a high destruction efficiency for most volatile organic compounds, resulting in the formation of carbon dioxide, water, and varying amounts of hydrogen chloride (from halogenated hydrocarbon derivatives). The presence in emissions of chemicals such as heavy metals, phosphorus, sulfur, chlorine, and most halogens in the incoming air stream act as poison to the system and can foul up the catalyst.

Thermal oxidation systems, without the use of catalysts, also involve chemical conversion (more correctly, chemical destruction) and operate at temperatures in excess of 815°C (1,500°F), or 220 to 610°C (395 to 1,100°F) higher than catalytic systems. There are many variables in treating gas streams. The precise area of application of a given process is difficult to define. Several factors must be considered, and these are (i) the types and concentration of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide and carbon dioxide, gas may contain other contaminants, such as mercaptans and carbonyl sulfide. The presence of these impurities may eliminate some of the sweetening processes, as some processes remove large amounts of acid gas but not to a sufficiently low concentration. However, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. These processes are also capable of removing the acid gas impurities to low levels when the acid gases are there in low-to-medium concentrations in the gas.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Catalytic Reforming

Like thermal reforming, *catalytic reforming* converts low-octane gasoline into high-octane gasoline (reformate) by rearranging hydrocarbon molecules in a gasoline-boiling-range feedstock to produce other hydrocarbon derivatives having a higher antiknock quality; isomerization of paraffins, cyclization of paraffins to naphthenes, dehydrocyclization of paraffins to aromatics.

Catalytic reforming uses catalytic reactions to process primarily low octane heavy straight run (from the crude distillation unit) gasoline and naphtha into high octane aromatics (including benzene). There are four major types of reactions which occur during reforming processes, and these are (i) dehydrogenation of naphthenes to aromatics, (ii) dehydrocyclization of paraffins to aromatics, (iii) isomerization, and (iv) hydrocracking. The dehydrogenation reactions are endothermic, requiring that the hydrocarbon stream be heated between each catalyst bed. All but the hydrocracking reaction release hydrogen which can be used in the hydrotreating or hydrocracking processes. Fixed-bed or moving bed processes are utilized in a series of three to six reactors.

Operating conditions are in the ranges of 425 to 530°C, 50 to 750 psig, 0.7 to 5.0 h⁻¹ space velocity, and 3.0 to 10.0 moles of gas per mole of naphtha, gas recycle ratio, depending upon the process type and catalyst employed.

Catalytic reforming is conducted in the presence of hydrogen over hydrogenation-dehydrogenation catalysts, which may be supported on alumina or silica-alumina. Depending on the catalyst, a definite sequence of reactions takes place, involving structural changes in the charge stock.

Catalytic reformer feeds are saturated (i.e., not olefin) materials; in the majority of cases, the feed may be a straight-run naphtha, but other by-product low-octane naphtha (e.g., coker naphtha) can be processed after treatment to remove olefins and other contaminants. Hydrocarbon naphtha that contains substantial quantities of naphthenes is also a suitable feed. The process uses a precious metal catalyst (platinum supported by an alumina base) in conjunction with high temperatures to reform the paraffin and naphthene constituents into high-octane components. Sulfur is a poison to the reforming catalyst, which requires that virtually all the sulfur must be removed from the heavy naphtha through hydrotreating prior to reforming. Several different types of chemical reactions occur in the reforming reactors: paraffins are isomerized to branched chains and to a lesser extent to naphthenes, and naphthenes are converted to aromatics. Overall, the reforming reactions are endothermic. The resulting product stream (*reformate*) from catalytic reforming has an RON from 96 to 102 depending on the reactor severity and feedstock quality. The dehydrogenation reactions which convert the saturated naphthenes into unsaturated aromatics produce hydrogen, which is available for distribution to other refinery hydroprocesses.

The catalytic reforming process consists of a series of several reactors which operate at temperatures of approximately 480°C (900°F). The hydrocarbon derivatives are re-heated by direct-fired furnaces in between the subsequent reforming reactors. As a result of the high temperatures, the catalyst becomes deactivated by the formation of coke (i.e., essentially pure carbon) on the catalyst which reduces the surface area available to contact with the hydrocarbon derivatives.

Catalytic reforming is usually carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace where the mixture is heated to the desired temperatures 450 to 520°C (840 to 965°F), and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100 to 1,000 psi. Normally, two (or more than one) reactors are used in series, and reheaters are located between adjoining reactors to compensate for the endothermic reactions taking place. Sometimes, as many as four or five are kept on-stream in series while one or more are being regenerated. The on-stream cycle of any one reactor may vary from several hours to many days, depending on the feedstock and reaction conditions.

The product issuing from the last catalytic reactor is cooled and sent to a high-pressure separator where the hydrogen-rich gas is split into two streams: one stream goes to recycle, and the remaining portion represents excess hydrogen available for other uses. The excess hydrogen is vented from the unit and used in hydrotreating, as a fuel, or for manufacture of chemicals (e.g., ammonia). The liquid product (reformate) is stabilized (by removal of low boiling products, often referred to as light ends) and used directly in gasoline or extracted for aromatic blending stocks for aviation gasoline.

Emissions from catalytic reforming include fugitive emissions of volatile constituents in the feed, and emissions from process heaters and boilers. As with all process heaters in the refinery, combustion of fossil fuels produces

emissions of sulfur oxides, nitrogen oxides, carbon monoxide, particulate matter, and volatile hydrocarbon derivatives.

Toluene, xylene, and benzene are toxic aromatic chemicals that are produced during the catalytic reforming process and used as feedstocks in chemical manufacturing. Due to their highly volatile nature, fugitive emissions of these chemicals are a source of their release to the environment during the reforming process. Point air sources may also arise during the process of separating these chemicals.

In a continuous reformer, some particulate and dust matter can be generated as the catalyst moves from reactor to reactor, and is subject to attrition. However, due to catalyst design, little attrition occurs, and the only outlet to the atmosphere is the regeneration vent, which is most often scrubbed with a caustic to prevent emission of hydrochloric acid (this also removes particulate matter). Emissions of carbon monoxide and hydrogen sulfide may occur during regeneration of catalyst.

See also: Refining.

Catalytic Reforming - Catalysts

The reforming catalyst is usually supplied as nickel oxide that, during start-up, is heated in a stream of inert gas, then steam. When the catalyst is near the normal operating temperature, hydrogen or a low-boiling hydrocarbon is added to reduce the nickel oxide to metallic nickel.

The high temperatures (up to 870°C, 1,600°F) and the nature of the reforming reaction require that the reforming catalyst be used inside the radiant tubes of a reforming furnace. The active agent in reforming catalyst is nickel, and normally, the reaction is controlled both by diffusion and by heat transfer. Catalyst life is limited as much by physical breakdown as by deactivation.

Sulfur is the main catalyst poison, and the catalyst poisoning is theoretically reversible with the catalyst being restored to near full activity by steaming. However, in practice, the deactivation may cause the catalyst to overheat and coke, to the point that it must be replaced. Reforming catalysts are also sensitive to poisoning by heavy metals, although these are rarely present in low-boiling hydrocarbon feedstocks and in naphtha feedstocks.

Coking deposition on the reforming catalyst and ensuing gloss of catalyst activity are the most characteristic issues that must be assessed and mitigated.

While methane-rich refinery gas streams are the most common feedstocks to hydrogen plants, there is often a requirement for a variety of reasons to process a variety of higher boiling feedstocks, such as liquefied petroleum gas and naphtha. Feedstock variations may also be inadvertent due, for example, to changes in refinery off-gas composition from another unit or because of variations in naphtha composition because of feedstock variance to the naphtha unit.

Thus, when using higher boiling feedstocks in a hydrogen plant, coke deposition on the reformer catalyst becomes a major issue. Coking is most likely in the reformer unit at the point where both temperature and hydrocarbon content are high enough. In this region, hydrocarbon derivatives crack and form coke faster than the coke is removed by reaction with steam or hydrogen, and when catalyst deactivation occurs, there is a simultaneous temperature increase with a concomitant increase in coke formation and deposition. In other zones, where the hydrocarbon-to-hydrogen ratio is lower, there is less risk of coking.

Coking depends to a large extent on the balance between catalyst activity and heat input with the more active catalysts producing higher yields of hydrogen at lower temperature thereby reducing the risk of coking. A uniform input of heat is important in this region of the reformer since any catalyst voids or variations in catalyst activity can produce localized hot spots leading to coke formation and/or reformer failure.

Coke formation results in hotspots in the reformer that increases pressure drop, and reduces feedstock (methane) conversion, leading eventually to reformer failure. Coking may be partially mitigated by increasing the steam/feedstock ratio to change the reaction conditions, but the most effective solution may be to replace the reformer catalyst with one designed for higher boiling feedstocks.

A standard steam-methane reforming catalyst uses nickel on an alpha-alumina ceramic carrier that is acidic in nature. Promotion of hydrocarbon cracking with such a catalyst leads to coke formation from higher boiling feedstocks. Some catalyst formulations use a magnesia/alumina ($\text{MgO}/\text{Al}_2\text{O}_3$) support that is less acidic than α -alumina that reduces cracking on the support and allows higher boiling feedstocks (such as liquefied petroleum gas) to be used.

Further resistance to coking can be achieved by adding an alkali promoter, typically some form of potash (KOH) to the catalyst. Besides reducing the acidity of the carrier, the promoter catalyzes the reaction of steam and carbon. While carbon continues to be formed, it is removed faster than it can build up. This approach can be used with naphtha feedstocks with boiling point up to approximately 180°C (350°F). Under the conditions in a reformer, potash is volatile and it is incorporated into the catalyst as a more complex compound that slowly hydrolyzes to release potassium hydroxide (KOH). Alkali-promoted catalyst allows the use of a wide range of feedstocks, but, in addition to possible potash migration, which can be minimized by proper design and operation, the catalyst is also somewhat less active than a conventional catalyst.

Another option to reduce coking in steam reformers is to use a *pre-reformer* in which a fixed-bed of catalyst, operating at a lower temperature, upstream of the fired reformer is used. In a pre-reformer, adiabatic steam-hydrocarbon reforming is performed outside the fired reformer in a vessel containing high nickel catalyst. The heat required for the endothermic reaction is provided by hot flue gas from the reformer convection section. Since the feed to the fired reformer is now partially reformed, the steam methane reformer can operate at an increased feed rate and produce 8 to 10% additional hydrogen at the same reformer load. An additional advantage of the pre-reformer is that it facilitates higher mixed feed preheat temperatures and maintains relatively constant operating conditions within the fired reformer regardless of variable refinery off gas feed conditions. Inlet temperatures are selected so that there is minimal risk of coking and the gas leaving the pre-reformer contains only steam, hydrogen, carbon monoxide, carbon dioxide, and methane. This allows a standard methane catalyst to be used in the fired reformer, and this approach has been used with feedstocks up to low-density kerosene. Since the gas leaving the pre-reformer poses reduced risk of coking, it can compensate to some extent for variations in catalyst activity and heat flux in the primary reformer.

See also: Refining.

Catalytic Reforming – Processes

The commercial processes available for use can be broadly classified as the moving-bed, fluid-bed, and fixed-bed types. The fluid-bed and moving-bed processes use mixed non-precious metal oxide catalysts in units equipped with separate regeneration facilities. Fixed-bed processes use predominantly platinum-containing catalysts in units equipped for cycle, occasional, or no regeneration.

There are several types of catalytic reforming process configurations that differ in the manner that they accommodate the regeneration of the reforming catalyst. Catalyst regeneration involves burning off the coke with oxygen. The semi-regenerative process is the simplest configuration but does require that the unit be shut down for catalyst regeneration in which all reactors (typically four) are regenerated. The cyclic configuration utilizes an additional swing reactor that enables one reactor at a time to be taken off-line for regeneration while the other four remain in service. The continuous catalyst regeneration (CCR) configuration is the most complex configuration and enables the catalyst to be continuously removed for regeneration and replaced after regeneration. The benefit to the more complex configurations is that operating severity may be increased as a result of higher catalyst activity but this does come at an increased capital cost for the process.

Under the high-hydrogen partial pressure conditions used in catalytic reforming processes, sulfur compounds are readily converted into hydrogen sulfide, which, unless removed, builds up to a high concentration in the recycle gas. Hydrogen sulfide is a reversible poison for platinum and causes a decrease in the catalyst dehydrogenation and dehydrocyclization activities. In the first catalytic reformers, the hydrogen sulfide was removed from the gas cycle stream by absorption in, for example, diethanolamine. Sulfur is generally removed from the feedstock by use of a conventional desulfurization over cobalt-molybdenum catalyst. An additional benefit of desulfurization of the feed to a level of <5 ppm sulfur is the elimination of hydrogen sulfide (H₂S) corrosion problems in the heaters and reactors.

The yield of gasoline of a given octane number and at given operating conditions depends on the hydrocarbon types in the feed. For example, high-naphthene stocks, which readily give aromatic gasoline, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization, and hydrocracking reactions, require more severe conditions and give lower gasoline yields than the naphthenic stocks. The end point of the feed is usually limited to approximately 190°C (375°F), partially because of increased coke deposition on the catalyst as the end point during processing at approximately 15°C

(27°F). Limiting the feed end point avoids redistillation of the product to meet the gasoline end-point specification of 205°C (400°F), maximum.

Moving-bed catalytic reforming processes employ a single, moving-catalyst-bed reactor with continuous catalyst regeneration but are no longer considered commercially practical.

The catalyst is a non-precious metal oxide mixture in bead or pellet form which is transported between reactor and regenerator by mechanical or other means. Depending upon catalyst type, typical feedstock for motor-gasoline usage has an initial boiling range of 65 to 80°C (150 and 175°F) and an end-point range of 200 to 215°C (390 and 420°F).

See also: Refining.

Catalytic Three-Phase Reactors

Catalytic three-phase reactors are of great industrial importance in the crude oil and petrochemical industries; they are also used in the manufacture of synthetic fuels. A common name for this kind of reactor is a slurry reactor or slurry phase reactor.

In the reactor, a gas phase, a liquid phase, and a solid catalyst phase coexist. Some of the reactants and/or products are in the gas phase under the prevailing conditions (temperature and pressure). The gas components diffuse through the gas-liquid interface, dissolve in the liquid, diffuse through the liquid film to the liquid bulk phase, and diffuse through the liquid film around the catalyst particle to the catalyst surface, where the chemical reaction takes place. If catalyst particles are porous, a chemical reaction and diffusion take place simultaneously in the catalyst pores – the product molecules are transported in the opposite direction.

The size of the catalyst particle is of considerable importance for catalytic three-phase reactors. Catalyst particles can be small and are suspended in the liquid phase. Catalyst particles of a size similar to those used in two-phase packed bed reactors can also be used in three-phase reactors. Small catalyst particles are mainly used in bubble columns, stirred tank reactors, and fluidized beds.

On the other hand, packed bed reactors are generally filled with much larger catalyst particles.

Catalytic Transesterification

Transesterification or alcoholysis is the process in which nonedible oil is allowed to chemically react with alcohol. In this reaction, methanol and ethanol are the most commonly used alcohols because of their low cost and availability. This reaction has been widely used to reduce the viscosity of nonedible oil and for the conversion of triglycerides into ester.

The catalyzed transesterification process can be classified into acid- and base- catalyzed processes. Depending on the nature of the catalyst phase, further, the acid or base catalyst can be divided into three subclasses such as homogeneous, heterogeneous, and enzymatic catalyst. The conversion efficiency of homogeneous-catalyzed transesterification is better when the free fatty acid derivative is less than 1 mg of KOH/g of oil. Two-step transesterification process is needed when the free fatty acid value is greater than 1 milligram of potassium hydroxide per gram (1 mg KOH/g) of oil.

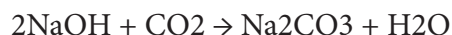
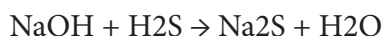
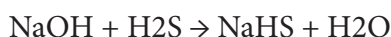
The process facilitates the recovery of the high amount of mixture of fatty esters, but it requires a high amount of alcohol to prevent the production of soap, which is an unwanted reaction. Enzymes (i.e., enzymatic reaction) can be used instead of catalysts, but the lipase enzymes that are mostly used in the enzymatic reaction are expensive; thus, the high cost makes the enzymatic reaction less effective than chemical reactions, and the reaction rate is slow and the productivity is low.

The main limitations of the use of a homogeneous catalyst are soap formation during the transesterification process and expensive separation of catalyst after the process. As a result, feedstocks which have a high free fatty acid content can be readily converted by the heterogeneous catalyst and heterogeneous and enzymatic catalysts are the best catalysts for the conversion of triglycerides into methyl esters. The heterogeneous catalyst has many advantages over homogeneous catalyst which are (i) easy removal of the catalyst, (ii) reusability, and (iii) easy purification.

See also: Transesterification.

Caustic Scrubbing

Hydrogen sulfide removal with caustic scrubbing is only economical when small amounts of hydrogen sulfide are present and suitable means of disposing the spent solution are available. All of the processes incorporate the same basic chemistry:



The SulphaCheck process uses sodium nitrite (NaNO_2) as the basis for the caustic process. Gas streams with elevated oxygen levels with the Sulfa Check process will produce some nitrogen oxides (NO_x) in the gas stream.

The reaction between sodium hydroxide and carbon dioxide occurs between gas streams in a scrubbing tower and can be inhibited by operating with low residence times. Absorption of hydrogen sulfide is not affected when the process operates with short contact times since the reaction is almost instantaneous.

Sodium hydroxide and sodium nitrite are consumables in the caustic-based processes and cannot be regenerated. If the waste effluent meets standards for sulfide content and iron content, it is reclaimable as a market commodity. However, in gas streams with high concentrations of carbon dioxide, the sodium carbonate concentration will be above the reclaimable limit and the effluent must be disposed.

The use of supercritical methanol, a noncatalytic transesterification process, is a way to solve the problems with catalytic transesterification. In this, the dielectric value of methanol is lowered by heating to supercritical temperature state to make a single phase of reactants. As a result, the overall reaction is to be completed in a short duration of time. Furthermore, the noncatalytic process requires no catalyst and purification is easier than the catalytic process. In this, there is no soap formation during the process. There is a limitation associated with supercritical methanol transesterification which is the expensive cost of equipment to attain the high temperature and pressure.

See also: Gas Treating.

Caustic Treating

Because of the variety of feedstock that are used to produce biogas and bio-liquids, it is inevitable that at some stage, a feedstock mat contains sulfur derivatives. These derivatives must be removed from the (gaseous or liquid) product in order for the final product to meet sales specifications and environmental regulations.

The caustic (caustic soda, NaOH , lye, potassium hydroxide, KOH) treating process is used to upgrade a wide range of fractions from liquefied petroleum gas, diesel fuel, and heating oils and finds ready use in treating biogas and bio-liquids, such as bio-oil. As the caustic solution (and often a catalyst) mixes with the feedstock, it either extracts or converts mercaptan derivative to less obnoxious products.

The process consists of mixing an aqueous solution of caustic with a product fraction as soon as possible after the fraction is distilled (or isolated) since contact with air forms free sulfur, which is very corrosive and difficult to remove from fuel-type products (or from fuel precursors). The caustic reacts with any hydrogen sulfide present to form sodium sulfide, which is soluble in water.

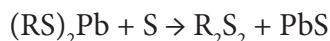
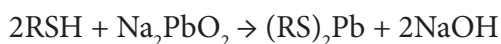
However, the combination of the feedstock and mercaptan-rich caustic also forms a very stable emulsion that is difficult to separate, causing significant quantities of caustic carry-over in the product. This results in off-specification products due to haze or elevated sodium concentration and loss of caustic. In many cases, the entrained caustic is fed to processes where sodium is a poison to the catalyst. Because the emulsion is so stable, knock-out drums, sand filters, and packed vessels are not able to efficiently separate the caustic emulsion from the hydrocarbon streams.

The refining industry has historically used caustic solutions to extract or treat acidic impurities in liquid hydrocarbon streams. A number of caustic processes, both regenerative and nonregenerative, can be used to remove sulfur

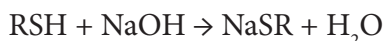
compounds from fuels or from precursors to fuels. The simplest process is the use of a nonregenerative solid potassium hydroxide (KOH) bed, which is effective for removal of H_2S but not for other sulfur compounds. One of the common processes for treating hydrocarbon liquids is the use of regenerative caustic wash with sodium hydroxide (NaOH). Typically, the caustic wash is located downstream of an amine unit, which is used for bulk acid gas removal which minimizes the treating duty required by caustic wash. When acid gas quantities are small, a simple caustic wash is effective and economical. However, as the quantity of contaminants increases, the caustic wash process can be expensive due to high chemical and disposal costs.

Several organic materials may be added to caustic solutions (as promoters) to increase their solubility for mercaptan derivatives. Mercaptans can be converted to disulfides by several methods. These disulfides will remain in the sweetened hydrocarbon product. The overall sulfur content, therefore, remains unchanged. However, the sulfur leaves as a disulfide derivative (typically odorless) rather than a mercaptan. The method or combination of methods that can be used depend on the mercaptan content of the product to be treated and the specification that must be met.

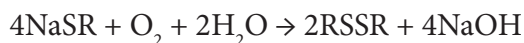
Among the processes that convert (oxidize) mercaptans to disulfides, the Doctor sweetening process is the earliest process. In this process, an alkaline solution of lead oxide (usually sodium plumbite) contacts the feedstock forming lead mercaptide derivatives (soluble in the oil) with the mercaptan derivatives. The mixture is then treated with powdered sulfur (which has a high affinity for lead), and a conversion of the mercaptide into a so-called disulfide (which remains in solution in the gasoline stream) occurs. The process chemistry can be represented by the following equations:



The Merox process is used to treat end-product streams by rendering any mercaptan sulfur compounds inactive. The method involves the extraction reaction of the sour feedstock containing mercaptans (RSH) with caustic soda (NaOH) in a single, multi-stage extraction column using high efficiency trays:



After extraction, the extracted mercaptans in the form of sodium mercaptides (NaSR) are catalytically oxidized to water-insoluble disulfide oils (RSSR):

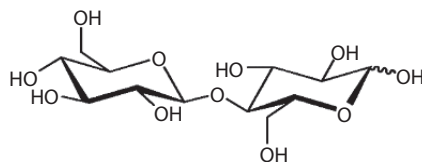


The disulfide oil is decanted and sent to fuel or to further processing in a hydrotreater. The regenerated (lean) caustic is then recirculated to the extraction column.

See also: Refining.

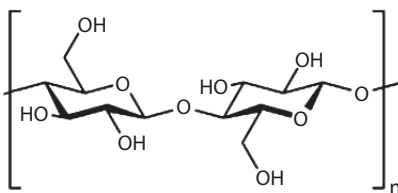
Cellulose

Cellulose (30 to 50% w/w of total feedstock dry matter) is a glucose polymer linked by β -1,4 glycosidic bonds. The basic building block of this linear polymer is cellubiose, which is a glucose-glucose dimer:



Cellubiose

Cellulose is an organic compound polysaccharide consisting of a linear chain of several hundred to over ten thousand linked D-glucose units and has the formula $(C_6H_{10}O_5)_n$.



Cellulose

The hydrolysis of cellulose (saccharification) produces its glucose monomers.

Cellulose is an important structural component of the primary cell wall of green plants, many forms of algae, and the oomycetes. Some species of bacteria secrete it to form biofilms. Approximately 33% of all plant matter is cellulose – the cellulose content of cotton is approximately 90% and that of wood is approximately 50% (Table C-1). On the other hand, cellulase refers to a class of enzymes produced by organisms such as fungi and bacteria that catalyze the hydrolysis of cellulose (cellulolysis).

Table C-1 Amount (% w/w) of cellulose and hemicellulose in various sources *.

Source	Cellulose	Hemicellulose
Bamboo	41-49	24-28
Cattle manure	1.6-4.7	1.4-3.3
Corn cobs	45	35
Corn stover	35	28
Grasses	25-40	35-50
Hardwood stem	40-50	24-40
Leaves	15-20	80-85
Newspaper	40-55	25-40
Nut shells	25-30	25-30
Paper	85-99	0
Rice straw	40	18
Softwood stem	45-50	25-35
Sugar cane bagasse	32-48	19-24
Sweet sorghum	27	25
Switch grass	30-51	10-50
Waste papers from chemical pulps	60-70	10-20
Wheat straw	33-40	20-25

* The wastes are listed alphabetically rather than in any other order.

Hemicellulose (20 to 40% w/w of total feedstock dry matter) is a short, highly branched polymer of five (C_5) and six-carbon (C_6) sugar derivatives. Specifically, hemicellulose contains xylose and arabinose (C_5 sugars) and galactose, glucose, and mannose (C_6 sugars). Hemicellulose is more readily hydrolyzed than cellulose because of its branched, amorphous nature, and a major product of hemicellulose hydrolysis is xylose (a C_5 sugar).

Cellulose is a potential biofuel source and compares favorably in terms of volatiles production with lignin and lignocellulose (Table C-2).

Table C-2 The ultimate and proximate analysis of cellulose, lignin, and lignocellulose.

Composition, %v/w	Cellulose	Lignin	Lignocellulose
Carbon	47.2	72.5	53.4
Hydrogen	5.8	5.4	5.4
Nitrogen	0.0	0.0	0.0
Sulfur	0.0	0.0	0.0
Oxygen	47.0	22.1	41.0
Proximate analysis, % w/w			
Moisture	4.3	2.6	9.4
Volatile matter (daf)	84.7	76.7	76.5
Fixed carbon (daf)	11.1	20.7	13.6
Ash (dry)	0.0	0.0	0.5
Note: daf = dry, ash free			

See also: Carbohydrates.

Cellulosic Biomass

The source of energy and serving point is cellulosic material, usually derived from evergreen trees that contain hemicellulose (35 to 45%), lignin (20 to 30%), and extractable materials (0 to 5%).

Cellulose is the main part of the cell wall, with the elementary formula $(C_6H_{10}O_5)_n$. It is a highly linear polysaccharide and similar to hemicellulose, but the latter has a more branched structure and is more susceptible to chemical degradation than cellulose. Lignin acts like the boundaries in the cells, and gives rigidity to the cell wall. They are complex three-dimensional polymers of phenylpropane.

The cellulosic biomass contains carbon (45 to 55 % w/w), hydrogen (5 to 7 % w/w), oxygen (40 to 50 % w/w), small amounts of sulfur (0 to 0.05 % w/w), and nitrogen (0 to 1.0 % w/w). The mineral matter content is also of importance (being converted to ash during processing) for the heating value – the heating value decreases with increasing ash content.

An important distinction in the field of wood processing is made between softwood and hardwood. The different density of the woods has influence on which technology to apply in the processing, as the density may differ considerably between different types of forest.

Another important parameter is the moisture content in the wood. As trees are dependent on water to grow, there is always a high content of water in recently chopped wood. As water evaporates, considerable amounts of energy are required and less energy is available. The moisture content is therefore a major element in deciding the effective heating value (EHV). The EHV is defined as the lower heating value (LHV) subtracting the energy of evaporating the moisture content of the wood. The LHV assumes that the produced water is 100% evaporated. The water might leave the process as liquid water and not as vapor. The resulting energy content is defined as higher heating value (HHV). The LHV has been used traditionally, and serve as the definition of energy content also in this study.

At moisture content of 87%, the energy content of the wood is the same as the required energy to evaporate the moisture. The critical limit is 50 to 55% moisture; further increased moisture content above this level lowers the energy content dramatically. But the moisture content should not always decrease to below a certain limit, as very dry biomass produces a synthesis gas with less hydrogen.

The EHV can be calculated as an approximation with the following formula [kWh/kg]:

$$\text{EHV} = 5.326.01m = - [\text{kWh/kg}]$$

In this equation, m is the moisture content, calculated as the relation between mass of water and total mass of wood and water.

The HHV (MJ/kg) may be calculated to a reasonable approximation from the molecular composition:

$$\text{HHV} = 0.3491 \cdot X_C + 1.1783 \cdot X_H + 0.1005 \cdot X_S - 0.0151 \cdot X_N - 0.1034 \cdot X_O - 0.0211 \cdot X_{\text{ash}}$$

It is evident how hydrogen and carbon atoms are contributing to the heating value, and how the oxygen content is contributing negatively. It is therefore an important step in some biomass conversion routes to deoxidize the biomass in order to increase the heating value.

See also: Carbohydrates, Cellulose.

Cellulosic Ethanol

The first category of ethanol production technologies falls under the rubric of cellulosic ethanol.

Wood is made up, for the most part, of only three chemicals, cellulose, hemicellulose, and lignin. Cellulose and, to a lesser degree, hemicellulose provide the structural strength of wood. They are long chain molecules consisting of smaller linked sugar molecules. Cellulose, particularly, has extremely high tensile strength and gives to wood its largely unmatched structural properties.

Lignin serves as a binder and holds the chains of cellulose and hemicellulose together. It is a very tough and chemically resistant material, which explains how wooden objects can survive for hundreds and even thousands of years.

Both cellulose and hemicellulose may be converted into sugars, though not the same sugars. Cellulose produces six carbon sugars such as glucose. Hemicellulose splits into five carbon sugars such as xylose. Lignin, which is not sugar-based, generally constitutes a waste product in the production of cellulosic alcohol though it may be burned to provide processing heat or to generate electricity.

Cellulose and hemicellulose can be separated from lignin by exposure to solvents, generally acids, or by the action of enzymes, of which cellulase is the most frequently used. The enzymatic processes fall into the category of enzymatic hydrolysis, while those using acids are known collectively as acid hydrolysis. Acid hydrolysis technologies are further divided into two subcategories, concentrated acid hydrolysis and dilute acid hydrolysis.

Cellulosic ethanol manufacturing techniques are limited in the feedstocks they can accept, but the potential exists for integration of the process with other industrial energy producing processes. Thus:

Starch → hydrolysis → sugars → fermentation → product recovery

Lignocellulosic biomass → thermochemical conversion → pyrolysis oil + synthesis gas

Most have difficulties in processing softwoods, which tend to have a high lignin content, and, unfortunately, most wood waste comes from softwood sources. Agricultural wastes such as rice straw and corn stover are preferred, though many authorities believe dedicated energy crops such as switch grass, laurel, miscanthus, etc., will predominate as production increases.

See also: Carbohydrates, Cellulose, Cellulosic Biomass.

Cellulosic Materials

Cellulose from wood, agricultural residue, waste sulfite liquor from pulp, and paper mills must first be converted to sugar before it could be fermented. Enormous amounts of carbohydrate-containing cellulosic wastes are generated every year throughout the world ethanol production. The technology for converting this material into ethanol is available, but the stoichiometry of the process is unfavorable. Approximately two-thirds of the mass disappears during the conversion of cellulose to ethanol, most of it as carbon dioxide in the fermentation of glucose to ethanol. This amount of carbon dioxide leads to a disposal problem rather than to a raw material credit. Another problem is that the aqueous acid used to hydrolyze the cellulose in wood to glucose and other simple sugars destroys much of the sugar in the process.

Of the cellulose materials, shavings, sawdust, and straw are used for fuel in some places. They are bulky and difficult to handle, while their heat value, which depends on the amount of moisture they contain, is seldom more than from one-third to one-half that of sub-bituminous coal. Such waste matter as spent tan-bark and bagasse (crushed sugar cane), and the pulp from sugar beets is sometimes used for fuel for evaporation for steam, but owing to the large amount of moisture they contain, the heat value is low.

The conversion of cellulosic wastes proceeds via a two-step process that involves (i) hydrolysis and (ii) fermentation with the two steps operated sequentially. The hydrolysis step is the more critical and rate-determining step, since in this process, step cellulose is transformed into glucose that is made available to the microbes responsible for the ethanol fermentation.

Among the several forms of cellulose hydrolysis (saccharification), the chemical and biological types are the most commonly applied. Because the actual hydrolysis is accomplished enzymatically, the biological hydrolysis is designated as enzymatic hydrolysis. Although the use of enzymes avoids the corrosion problems and the loss of fuel product associated with acid hydrolysis, enzymes have their own drawbacks. Enzymatic hydrolysis slows as the glucose product accumulates in the reactor vessel. The end product inhibition eventually halts the hydrolysis unless some way is found to draw off the glucose as it is formed.

See also: Carbohydrates, Cellulose, Cellulosic Biomass.

Centrifugal Separation

In the process known as sedimentation, two immiscible liquids, or a liquid and a solid, differing in density, are separated by allowing them to come to equilibrium under the action of gravity, the heavier material falling with respect to the lighter material. This process may be accelerated by applying centrifugal forces to increase the rate of sedimentation; this is called centrifugal separation.

Typically, the centrifuge consists of a horizontal revolving shell or bowl, cylindroconical in form, inside which a screw conveyor of similar section rotates in the same direction at a slightly higher or lower speed. The feed pulp is admitted to the bowl through the center tube of the revolving-screw conveyor. When it leaves the feed pipe, the slurry is immediately subjected to a high centrifugal force, causing the solids to settle on the inner surface of the bowl at a rate which depends on the rotational speed employed – typically between 1,600 and 8,500 revolutions per minute (rev min^{-1}). The separated solids are conveyed by the scroll out of the liquid and discharged through outlets at the smaller end of the bowl. The solids are continuously dewatered by centrifugal force as they proceed from the liquid zone to the discharge. Excess entrained liquor drains away to the pond circumferentially through the particle bed. When the liquid reaches a predetermined level, it overflows through the discharge ports at the larger end of the bowl.

The centrifugal force depends upon the radius and speed of rotation and upon the mass of the particle. If the radius and the speed of rotation are fixed, then the controlling factor is the weight of the particle so that the heavier the particle, the greater the centrifugal force acting on it. Consequently, if two liquids, one of which is twice as dense as the other, are placed in a bowl and the bowl is rotated about a vertical axis at high speed, the centrifugal force per unit volume will be twice as great for the heavier liquid as for the lighter. The heavy liquid will therefore move to occupy the annulus at the periphery of the bowl, and it will displace the lighter liquid toward the center.

Thus, centrifugal separation method employs centrifugal acceleration (up to one million times higher than the gravitational acceleration on earth) resulting from rotation in order to separate particles in a solution, as based on differences in sedimentation. The sedimentation of particles is influenced by both particle size and density, as well as by solution density and viscosity. Also, centrifugal separation can be regarded as an extension of gravity separation, as the settling rates of particles are increased under the influence of centrifugal force. It can, however, be used to separate emulsions which are normally stable in a gravity field.

See also: Cyclone Separation, Gas Cleaning, Gas Processing, Gas Treating, Particulate Matter Removal.

Cetane Index

The cetane index is an approximation of the cetane number calculated from the density and mid-boiling point temperature, and the ignition quality of diesel fuel can also be estimated from the following formula:

$$\text{Diesel index} = (\text{aniline point (oF)} \times \text{API gravity})100$$

The cetane index is calculated based on the fuel's density and boiling range. There are two methods used: ASTM D976 or ASTM D4737. These methods are particularly suitable for straight-run fuel, catalytically cracked stocks, and blends of the two. The correlation is best for these fuels and least satisfactory for blends containing substantial proportions of thermally cracked stocks. Neither of these standards is suitable for fuel containing pure hydrocarbons, or non-crude oil-based fuels derived from biomass. In addition, these methods take no account of cetane improvers used to raise the cetane number.

Standard test method ASTM D976 uses two variable equations to determine the calculated cetane index. Thus:

$$\text{CI}_{97} = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803(\log B)^2$$

D is the density at 15°C [g/mL] determined by Test Method ASTM D 1298, and B is mid-boiling temperature [°C] determined by Test Method ASTM D 86 and corrected to standard barometric pressure.

Standard test method ASTM D 4737 calculates cetane index using a four-variable equation based on diesel's low, mid, and high boiling points as well as density. Thus:

$$\text{CI}_{4737} = 45.2 + 0.0892T_{10N} + [0.131 + 0.901B]T_{50N} + [0.0523 + 0.420B]T_{90N} + 0.00049[T_{210N} - T_{290N}] + 107B + 60B^2$$

D is the density at 15°C [g/mL] determined by Test Method ASTM D 1298, B is the $[e(-3.5)(D - 0.85)]^{-1}$, $T_{10} = 10\%$ distillation temperature [°C] determined by Test Method ASTM D 86 and corrected to standard barometric pressure, $T_{10N} = T_{10} - 215$, $T_{50} = 50\%$ distillation temperature [°C] determined by Test Method ASTM D 86 and corrected to standard barometric pressure, $T_{50N} = T_{50} - 260$, $T_{90} = 90\%$ distillation temperature [°C] determined by Test Method ASTM D 86 and corrected to standard barometric pressure, $T_{90N} = T_{90} - 310$.

Cetane Number

The cetane number is a measure of the tendency of a diesel fuel to knock in a diesel engine. The scale is based upon the ignition characteristics of two hydrocarbons n-hexadecane (cetane) and 2,3,4,5,6,7,8-heptamethylnonane. Cetane has a short delay period during ignition and is assigned a cetane number of 100; heptamethylnonane has a long delay period and has been assigned a cetane number of 15. Just as the octane number is meaningful for automobile fuels, the cetane number is a means of determining the ignition quality of diesel fuels and is equivalent to the percentage by volume of cetane in the blend with heptamethylnonane, which matches the ignition quality of the test fuel (ASTM D613).

The cetane number is a measure of the ignition quality of a diesel fuel. It is often mistaken as a measure of fuel quality. Cetane number is actually a measure of a fuel's ignition delay. This is the time period between the start of injection and start of combustion (ignition) of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. The cetane number should not be considered alone when evaluating diesel fuel quality. API gravity, BTU content, distillation range, sulfur content, stability, and flash point are also important. In colder weather, cloud point and low temperature filter plugging point may be critical factors.

The optical method for determining cetane number (ASTM D613) requires the use of an industry standard test engine equipped with accepted instrumentation and operated under specific conditions. In this test, the engine compression ratio is varied for the test sample and reference fuels of known cetane number to obtain a fixed ignition delay. The compression ratio of the sample is bracketed by those of two reference fuels. The cetane number of the sample fuel is determined by estimating between the two reference fuel points.

There is no benefit to using a higher cetane number fuel than is specified by the engine's manufacturer. The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. Increase in cetane number over values actually required does not materially improve engine performance.

Diesel fuels with a cetane number lower than minimum engine requirements can cause rough engine operation. They are more difficult to start, especially in cold weather or at high altitudes. They accelerate lube oil sludge formation. Many low cetane fuels increase engine deposits resulting in more smoke, increased exhaust emissions, and greater engine wear.

Char

Char is the solid material that remains after low molecular weight gases, volatile liquids, and volatile tar have been driven out or released from a carbonaceous material, during the initial stage of thermal decomposition, such as happens during combustion or in carbonization processes. The process may also be referred to as devolatilization.

Biochar (biomass char) is the solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment. Biochar is a stable solid that is rich in carbon and can endure in the soil for millennia. Biochar may increase soil fertility of acidic soil (low pH soil) and increase agricultural productivity.

The physical and chemical properties of biochar is determined by the properties of the feedstock and the technology used to create the biochar. The properties of biochar can be characterized in several respects, including the proximate and elemental composition, pH value, and the porosity which correlate with different biochar properties. The atomic ratios of biochar, including the atomic hydrogen-to-carbon (H/C) and the atomic oxygen-to-carbon (O/C), correlate with the biochar properties that are relevant to the organic content such as polarity and aromaticity. In the carbonization process, both the atomic hydrogen-to-carbon (H/C) and the atomic oxygen-to-carbon (O/C) decreases due to the release of functional groups which contain hydrogen and oxygen.

See also: Biochar, Charcoal and Charcoal Briquettes.

Charcoal and Charcoal Briquettes

Charcoal is the blackish residue consisting of impure carbon obtained by pyrolytically removing water and other volatile constituents from animal and vegetation substances. Charcoal is usually produced by heating wood, sugar, bone char, or other substances in the absence of oxygen. The soft, brittle, lightweight, black, porous material contains 85% to 98% W/W carbon, extractable non-volatile tar, and mineral matter.

Historically, production of wood charcoal in districts where there is an abundance of wood dates back to a very remote period, and generally consists of piling billets of wood on their ends so as to form a conical pile, openings being left at the bottom to admit air, with a central shaft to serve as a flue. The whole pile is covered with turf or moistened clay. The firing is begun at the bottom of the flue, and gradually spreads outwards and upwards. The success of the operation depends upon the rate of the combustion, but generally, wood yields approximately 25% w/w charcoal but this yield is very dependent on the type of wood.

The modern process of carbonizing wood, either in small pieces or as sawdust in cast iron retorts, is extensively practiced where wood is scarce, and also for the recovery of valuable by-products (wood spirit, pyroligneous acid, wood tar), which the process permits. The question of the temperature of the carbonization is important; charcoal produced made at 300°C (570°F) is brown, soft and friable, and readily inflames at 380°C while charcoal; made at higher temperatures, it is hard and brittle, and does not fire until heated to approximately 700°C (1,290°F).

Commercial charcoal is found in lump, briquette, or extruded forms, thus (i) lump charcoal, which is made directly from hardwood material and usually produces far less ash than briquettes, (ii) briquettes, which are produced by compressing charcoal, typically made from sawdust and other wood by-products, with a binder (usually starch) and other additives, and (iii) extruded charcoal, which is made by extruding either raw ground wood or carbonized wood into logs without the need for a binder since the heat and pressure of the extruding process hold the charcoal together (Table C-3).

Table C-3 Characteristics of charcoal briquettes.

	Lump Charcoal	Briquettes	
		Without Filler	With Filler
Ash, % w/w	3-4	8	25
Moisture, % w/w	5	5	5
Carbon, % w/w	Balance	Balance	Balance
Volatiles, % w/w	10-15	10-15	10-15
Binder, % w/w	-	10	10
Calorific value, kJ/Kg	28,000	25,000	22,000
Btu/lb	12,050	10,750	9,500

Animal charcoal or bone black is the carbonaceous residue obtained by the dry distillation of bones; it contains only approximately 10% carbon, the remainder being calcium and magnesium phosphates (80%) and other inorganic material originally present in the bones. It is generally manufactured from the residues obtained in the glue and gelatin industries.

Charcoal fines have a much lower purity than lump charcoal and, in addition to charcoal, contain fragments, mineral sand and clay picked up from the earth and the surface of the wood and its bark. The fine-powdered charcoal (produced from bark, twigs, and leaves) has higher ash content than normal wood charcoal. Most of this undesired high ash material can be separated by screening the fines and rejecting undersized material passing, say, a 2- to 4-mm screen.

Briquetting requires a binder to be mixed with the charcoal fines, a press to form the mixture into a cake or briquette which is then passed through a drying oven to cure or set it by drying out the water so that the briquette is strong enough to be used in the same burning apparatus as normal lump charcoal.

Charcoal needs the addition of a sticking or agglomerating material to enable a briquette to be formed. The binder should preferably be combustible, though a non-combustible binder effective at low concentrations can be suitable. Starch is preferred as a binder though it is usually expensive. Tar and pitch from coal distillation or from charcoal retorts have been used for special purpose briquettes, but they must be carbonized again before use to form a properly bonded briquette.

The binders which have been tried are many, and the most common effective binder is starch. Approximately 4 to 8% of starch made into paste with hot water is adequate. First, the fines are dried and screened. Undersized fines are rejected and oversized hammer-milled. This powder is blended with the starch paste and fed to the briquetting press, and the resulting briquettes are dried in a continuous oven at approximately 80°C (176°F). The starch sets through loss of water, binding the charcoal into a briquette which can be handled and burned like ordinary lump charcoal in domestic stoves and grates. Briquettes bonded with tar or pitch and subsequently carbonized in charcoal furnaces to produce a metallurgical charcoal briquette of adequate crushing strength are needed.

Charcoal fines when available in large quantities do have industrial uses such as in metallurgical and calcining operations. For example, in charcoal iron making, fine charcoal can be injected at the base of the blast furnace with the air blast. Fine charcoal is excellent for producing sinter, partially reduced iron ore, to provide a high-grade feed to the blast furnace. This is one of the best ways to use charcoal fines as the amount which can be used is not limited to a percentage of the total as is the case of injection into the base of the blast furnace. Pulverized fine and lump charcoal can be burned in rotary furnaces producing cement clinker and calcium bauxite.

See also: Carbonization, Char.

Chemical Composition of Biomass

The chemical characteristics of biomass affect a variety of different processes. The chemical composition of the organic component of plant biomass is particularly important for microbial fermentation, pyrolysis, and gasification. The non-combustible constituents of biomass supplies greatly affect biomass combustion processes. The overall chemical constituents are similar for most plant materials. Plant cell walls consist of water and complex carbohydrates, particularly cellulose and hemicellulose. Lignin is a non-carbohydrate plant component, the highly cross-linked polymer “mortar” that binds the plant-cell bricks together to add to the plant’s structure as it matures. The cellulose, hemicellulose, and lignin portions of the vegetable matter in terrestrial plants are also referred to as the lignocellulosic complex. These components along with proteins, gums and resins, and ash-forming minerals make up the plant’s chemical structure.

The relative proportions of cellulose, hemicellulose, and lignin vary widely in proportion between softwoods, hardwoods, and herbaceous plants. Woody plants typically consist of approximately 50% w/w cellulose, 25% w/w hemicellulose, 25% w/w lignin, and trace amounts of ash-forming minerals. Herbaceous plants may contain approximately 40% w/w cellulose, 25% w/w hemicellulose, 15% w/w lignin, 5% w/w minerals, and 15% w/w proteins plus resins. The chemical composition of biomass feedstocks varies according to plant type but also by plant part (i.e., leaves, twigs, bark, stems, and roots). Variation in the proportion of different plant types and plant part components affects a variety of biomass conversion processes. Hardwood tree species tend to contain more hemicellulose and less lignin than softwoods. Grasses contain more volatile compounds in the form of proteins, fats, and resins than other herbaceous and woody plants.

The chemical characteristics of cellulose biomass are particularly important in combustion processes. Therefore, these characteristics are important to the decision process for choosing combustion technologies. While energy content is affected by the carbohydrate content in the plant material, the non-combustible fraction is particularly important for combustion because of operational issues associated with boiler efficiency, boiler slagging and fouling, erosion and corrosion, combustion instability, and particulate carry-over.

The amount of boiler slagging and fouling largely depends on the fusion temperature of the ash and the abundance and composition of ash-forming minerals. Slagging occurs when alkaline deposits accumulate or ash clumps together on the surfaces inside boilers. Alkalis such as sodium (Na) and potassium (K) are the primary causes of boiler slagging and typically have low melting points, reducing the ash fusion temperature. High alkalinity also causes fouling and slagging in stoker-type boilers and agglomeration in fluidized bed combustors (consumption of fluidized bed material along with biomass fuels). Typically, agricultural residue has higher alkalinity than does wood residue.

The value of pounds of alkali per million Btu (lb/MMBtu) can be used as an indicator to estimate the risk of boiler slagging and fouling problems. Research indicates that biomass fuels with alkali contents below 0.4 lb/MMBtu are not likely to cause slagging problems. Consequently, biomass feedstocks with high alkalinity are often blended with other fuels to reduce alkali concentrations to control fouling and slagging problems.

The minerals that combine to form ash have no energy value, so the HHV of a feedstock generally decreases as the ash content increases, reducing boiler efficiency. The ash content of a biomass feedstock should be analyzed to assess these impacts and estimate the amount of ash requiring disposal. Usually, clean softwood and hardwood fuels contain only trace amounts of ash-forming minerals, but cereal straws such as rice straw may have ash contents above 15% to 20%. Silica (SiO_2) is an abundant ash-forming mineral in crop residues that is abrasive, buffers acid reactions in pretreatment processes, and adds to slagging problems in boilers. Because the abundance of ash-forming minerals varies widely between woody and herbaceous plants and among plant components such as bark, leaves, and stems, full characterization of the feedstock will ensure appropriate conversion process design.

It is important to analyze the sulfur content of the feedstock to estimate the amount of sulfur oxides (SO_x) likely to occur in fuel emissions. In addition to polluting the atmosphere, sulfates form deposits on boiler convection tubes, contributing to slagging problems.

Overall, biomass has lower sulfur content and particulate emissions than coal, so biomass utilization benefits the environment by reducing the emissions of SO_x and ash associated with coal-fired boilers.

Chemical Precipitation

Chemical precipitation uses the addition of chemicals to convert a soluble component in a liquid feed into an insoluble solid material which can then be removed from the solution by filtration, flotation, or settling. The process is widely used for the removal of dissolved toxic metals as insoluble metal salts.

Chemical precipitation is also used as a pretreating technique for aqueous wastes destined for biological treatment. Such treatment can be done in either an on-site plant or publicly owned treatment works (POTW). The process can be used to remove heavy metals and toxic materials which are above the limits allowed for feed to the biological creating plant. The commonest forms of anions used to form the insoluble metal salts are hydroxides from the addition of lime (CaO) or caustic (NaOH) and sulfides from the addition of ferrous sulfide (FeS).

The metals that can be precipitated from aqueous wastes in an insoluble form include arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc. It is important to note that these metals are not present as elemental metal dissolved in the wastes, but are metallic ions from soluble dissociated metal salts. They can react with appropriate anions to generate insoluble particles of precipitate. The two most generic anions for metal precipitation are hydroxides and sulfides. However, as mentioned above, other specific anions are often used when metal recovery is the objective of treatment or only a single metal is present in the waste.

Hydroxide Precipitates

Most metals can be precipitated as hydroxides or oxides at high pH. The hydroxide precipitates are formed by adding hydroxide ions from lime or caustic soda to the waste stream. Among the divalent metal ions which precipitate as hydroxides are cadmium, copper, iron, lead, mercury, nickel, tin, and zinc. Ions which precipitate as trivalent hydroxides are aluminum, chromium, bismuth, gold, iron, antimony, and titanium. Silver I, copper I, and thallium IV can also be precipitated as hydroxide derivatives.

The reason for giving the effective pH range for precipitation of different cations is that many of the metal hydroxides are amphoteric. That is, they can act as either bases or acids. The metal serves as cation in the bases and as part of the anion in the acids. In the presence of sufficiently strong bases (i.e., at high pH), the metal hydroxides may redissolve, thus eliminating the hydroxide precipitate.

Sulfide Precipitates

Compared to hydroxide derivatives, sulfide derivatives have both advantages and disadvantages as a precipitant for metals. The major advantages are that sulfides have a lower solubility in water than hydroxides and do not have a pH-sensitive minimum which gives better metals removal and avoids redissolution of metals at high pH since the sulfides are not amphoteric.

The primary disadvantages to precipitation of metals as metal sulfides are (i) the potential for forming toxic hydrogen sulfide gas upon addition of sulfide chemicals to the metal-containing waste and (ii) the possibility of leaving excessive sulfide in the effluent, which would then require posttreatment. As in all these chemical treatments, some excess reagent is required to guarantee completeness of the desired reaction. However, the disadvantages of sulfide precipitation can be effectively avoided when adding sulfide as soluble salts such as sodium sulfide or bisulfide. However, the addition must be done in a closed system with adequate ventilation, and the sulfide dosage must be carefully controlled by using a sulfide-specific ion electrode to measure free sulfide. This system is capable of maintaining a free sulfide concentration of 0.5 ppm.

Also, ferrous sulfide, which is only slightly soluble in aqueous streams, is an effective sulfide precipitant. It is soluble enough to precipitate other heavy metals, but its own solubility is low enough to maintain a low free sulfide concentration which essentially eliminates the hydrogen sulfide problem in the reaction tank and ensures a low

concentration of soluble sulfide in the effluent. Unfortunately, ferrous sulfide is unstable and must be made on-site which also requires the same precautions against hydrogen sulfide generation during its preparation.

Specific Metal Precipitates

In addition to hydroxide derivatives and sulfide derivatives, a variety of precipitation agents can be used when specific metals are required to be recovered from a waste stream.

For example, cadmium and lead can be precipitated as carbonates at near neutral pH with a large attendant saving in base over hydroxide precipitation. Sodium borohydride (NaBH_4), a strong reducing agent, can be used to precipitate a variety of metal ions as elemental metals. They form a dense sludge, which can be sent to metals recovery for recycling of the metal. Sodium borohydride is especially effective for the precious metals industry, where the product is of exceptionally high value. The use of sulfate to precipitate barium and chloride to precipitate silver are classical analytical methods. Finally, the use of phosphate as a precipitant permits iron, chromium, and aluminum to be removed selectively from mixed wastes containing lower valence metal ions.

See also: Coagulation, Sedimentation.

Chemical Reaction Rates

Thermodynamics describes the energy requirements of a reaction; the speed at which it progresses is termed kinetics. It is important to be able to control the rate of chemical reactions for commercial and safety reasons. If a reaction takes too long to progress, the rate at which a product is manufactured would not be viable. Alternatively, if reactions progress too fast and 'run away' out of control, there could be dangers such as explosions. The rate at which reactions take place can be affected by the concentration of reactants, pressure, temperature, wavelength and intensity of light, size of particles of solid reactants, or the presence of catalysts (i.e., substances which alter the speed of reactions without being consumed during the reaction) or impurities.

The rate equation for a chemical reaction is an equation that links the reaction rate with concentrations or pressures of reactants and constant parameters. Typically, the reaction rate, r , is given by:

$$r = k[A]^x[B]^y$$

In this equation, $[A]$ and $[B]$ express the concentration of the species A and B, respectively (usually in moles per liter, M). The exponents x and y are the partial reactions orders and are determined experimentally – for some reactions, these exponents may not be equal to the stoichiometric coefficients. The constant k is the reaction rate constant (*rate coefficient*) of the reaction, and the value of this coefficient typically depends on the reaction parameters such as temperature.

Catalysts tend to be specific to a particular reaction or family of reactions. Thus, nickel is used to facilitate hydrogenation reactions (e.g., add hydrogen to $\text{C}=\text{C}$ double bonds) whereas platinum is used to catalyze certain oxidation reactions. Sometimes, care is needed with the purity of reactants since impurities can act as unwanted catalysts; alternatively, catalysts can be inactivated by *poisoning*.

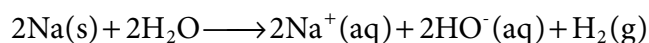
For reactions which progress slowly at room temperature, it may be necessary to heat the mixture or add a catalyst for the reaction to occur at an economically-viable rate. For fast reactions, the mixture may need to be cooled or solvent added to dilute the reactants and hence reduce the speed of reaction to manageable proportions. In general, the rate of a chemical reaction (i) doubles for every 10°C – 18°F rise in temperature, (ii) is proportional to the concentration of reactants in solution, (iii) increases with decreased particle size for reactions involving a solid, and (iv) increases with pressure for gas phase reactions.

Chemicals Reactive with Water

Chemical that are reactive with water (water-reactive chemicals) are substances are that reactive and dangerous when wet because of a chemical reaction with water. This reaction may release a gas that is either flammable or

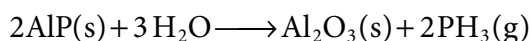
presents a toxic health hazard or both. In addition, the heat generated when water contacts such materials is often enough for the item to spontaneously combust and even explode. These chemicals can pose a threat to any operation in which chemicals are required to improve the process.

Examples of water-reactive chemicals are the alkali metals, the alkaline earth metals, anhydrides, carbides, hydrides, sodium hydrosulfite, and similar chemicals. An example of the chemical reaction of sodium metal with water is:



The heat generated by this reaction is generally sufficient to ignite the hydrogen gas (H_2) that is evolved in the reaction and can result in an explosion, depending on the amount and surface area of the alkali metal. Elemental potassium and cesium are particularly dangerous in this regard.

Another example of a dangerous when wet substance is aluminum phosphide (AlP) which reacts with water to release highly toxic phosphine gas, PH_3 . This chemical reaction is commercially exploited to kill moles and related pests:



Thus, it is critical that water reactive substances be stored in dry areas and kept off the floor by the use of pallets or rack storage. Dangerous when wet materials should never be stored directly beneath active water sprinklers and should be isolated by a waterproof or water-resistant barrier (e.g., plastic sheeting or a water-tight secondary container) to protect the materials from water in the event the sprinkler system is activated elsewhere in the facility.

Water-reactive chemical pose serious safety and health risks. The MSDS (material safety data sheet) will provide information about these risks as well as the precautions that should be taken when handling the material. Laboratory personnel should ensure that water-reactive materials are well-marked so that fire fighters and other personnel are aware of the danger in an emergency situation and be sure to have the correct type of fire extinguisher on hand.

Chemical Treating

Chemical treating is used to remove or change the undesirable properties associated with sulfur, nitrogen, or oxygen compound contaminants in crude oil products. Chemical treating is accomplished by either extraction or oxidation (sweetening), depending upon the product. Extraction is used to remove sulfur from the low-boiling fractions of crude oil, such as propane/propylene (PP) and butane/butylene (BB). Sweetening, though, is more effective on gasoline and middle distillate products.

A typical extraction process is Merox extraction. Merox extraction is used to remove mercaptans (organic sulfur compounds) from propane/propylene and butane/butylene streams. Propane/propylene streams may undergo amine treating before the Merox extraction to remove excess hydrogen sulfide which tends to fractionate with propane/propylene and interferes with the Merox process. A caustic prewash of the propane/propylene removes any remaining trace hydrogen prior to Merox extraction.

The propane/propylene and butane/butylene streams are passed up through the trays of an extraction tower. Caustic solution flowing down the extraction tower absorbs mercaptan from the propane/propylene and butane/butylene streams. The rich caustic is then regenerated by oxidizing the mercaptans to disulfide in the presence of aqueous Merox catalyst and the lean caustic recirculated to the extraction tower. The disulfide is insoluble in the caustic and can be separated.

Oxidation (Merox sweetening) is also used on gasoline and distillate fractions and uses a solid catalyst bed. Air and a minimum amount of alkaline caustic are injected into the hydrocarbon stream. As the hydrocarbon passes through the Merox catalyst bed, sulfur mercaptans are oxidized to disulfide. In the process, the caustic is not regenerated. Before the introduction of stricter sulfur regulations, the disulfide was allowed to remain in the gasoline

product, since it does not possess the objectionable odor properties of mercaptans; hence, the product has been sweetened.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Chemical Waste

A chemical waste is any solid, liquid, or gaseous waste material that can arise from any energy source – non-renewable or renewable – which, if improperly managed or the disposal method is inappropriate or faulty, may pose substantial hazards to human health and the environment.

More generally, chemical waste is a term and covers many types of materials but is generally recognized as a waste that is composed of harmful chemicals. Thus, by this definition, organic chemical waste is composed of harmful chemicals. The wastewater treatment industry describes sludge as a waste stream resulting from wastewater treatment. This description does not provide a physical or chemical basis for a definition but is adequate for the needs of wastewater treatment plant (WWTP) operations (i.e., anyone can distinguish between the treated effluent, which flows out of the plant, and the material that is pumped, scraped, or skimmed from the treatment units).

However, this definition of sludge, although adequate for the wastewater treatment industry, is inadequate for distinguishing between waste forms because it is qualitative and it ties the designation of sludge to its origins in wastewater treatment and, in this, two materials with identical characteristics may be defined as sludge or as liquid (i.e., treated effluent) based on facility-specific treatment processes and regulatory requirements governing the off-site discharge of the effluent. In order to develop a quantitative definition of sludge which will also help with correlating waste forms with disposal options, a simple and measurable characteristic of all three waste forms needs to be identified. One option is to define sludge on the basis of the solids content.

If the waste is an aqueous solution, the type and composition of the liquid waste depend on the source. In urban areas, the main sources are households, commercial establishments, and industries. Accurate information is needed related to the characteristics of liquid wastes in order to establish proper waste management processes to deal with them. The composition of liquid waste, also known as wastewater, is highly varied and depends principally on its source. In towns and cities, the three main sources are residential, commercial, and industrial areas. This is particularly true if the liquid waste is classed as a hazardous waste.

However, all chemical wastes are not hazardous wastes and an organic chemical waste may or may not be classed as hazardous waste. In terms of fuels from non-renewable and renewable sources, an organic chemical hazardous waste is a gaseous, liquid, or material that displays either a *hazardous characteristic* or is specifically listed by name as a hazardous waste. There are four characteristics by which chemical wastes may have to be considered as hazardous: (i) ignitability, (ii) corrosivity, (iii) reactivity, and (iv) toxicity. This type of hazardous waste must be categorized as to its identity, constituents, and hazards so that it may be safely handled and the disposal method defined.

At any stage of the management process, a chemical waste may be designated by law as a *hazardous waste*. Improper disposal of these waste streams, such as organic solvents, in the past has created hazards to human health and the need for expensive cleanup operations. Correct handling of these chemicals, as well as dispensing with many of the myths related to chemical processing, can mitigate some of the problems, especially problems related to the flammability of organic liquids, that will occur when incorrect handling is practiced.

See also: Sludge.

Chemicals from Biomass

While the concept of exploiting the wide range of chemicals from biomass may appear novel, the published literature shows that large numbers of metabolites have already been identified and characterized from a wide variety of plant species (Table C-4).

Table C-4 Examples of the chemicals that can be obtained from lignocellulosic biomass.

Starter	Intermediate	Products*
Cellulose	C1	Carbon dioxide
		Ethanol Formic Acid
		Synthesis gas
		Methane
	C2	Acetic acid
		Glycol aldehyde
	C3	Glyceraldehyde
		Hydroxy acetone
		Lactic acid
	C4	Erythrose
		Maleic acid
	C5	Furfural
		Levulinic acid
	C6	Fructose
		Mannitol
		Sorbitol
Hemi-cellulose	Xylose	Pentanoic acid
		Pentanol
		Furfural
Lignin	Phenols	Alcohols
		Hydrocarbons

*Listed alphabetically.

In fact, lignocellulosic biomass can be used as a source of chemicals that have a wide range of chemical, physical, and biological properties and include phenolics, nitrogen-containing compounds, and terpenes (terpenoids) and would be suitable for production in a biorefinery (Table C-5). The variety of molecular compounds is vast. For example, in the terpene group, there are six sub-groupings of molecules with a large number of applications including use in anti-cancer drugs.

Extraction procedures can have a major impact on the availability of these chemicals, and, to ensure optimal exploitation, some of the well-established extraction procedures may need to be revised. For example, in winter rapeseed, the harvested seed is crushed and the rapeseed oil extracted mechanically. The residual meal is then treated with hexane to extract the remaining oil, before being used as feed, primarily for ruminants. Rapeseed oil components have numerous applications including use in bio-diesel, and specialty chemicals.

Table C-5 Routes for the production of chemicals in a biorefinery.

Starter	Process	Intermediate	Process	Product
Lignocellulose	Hydrolysis	Cellulose	Catalytic hydrodeoxygenation	Biofuels
			Dehydration	Furfurals
			Fermentation	Alcohols
				Hydrogen
		Hemicellulose	Aqueous phase reforming	Hydrogen
				Hydrocarbons
			Dehydration	Biofuels
				Furfurals
			Fermentation	Alcohols
				Biofuels
		Lignin	Chemical conversion	Aromatics
				Dibasic acids
				Olefins
				Phenols

However, innovative oil-extraction procedures could allow greater exploitation of protein-based metabolites in the rapeseed, which can comprise 25% or more of the rapeseed mass. Research from studies, such as the Enhance project – funded by the European Community – has demonstrated that this separation would allow products to be produced for numerous applications (see diagram) with base cellulose material and some other metabolites remaining in the residual meal.

See also: Biochemicals.

Chemisorption

Chemisorption (chemical absorption) is a type of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the surface of the adsorbent. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds. Due to specificity, the nature of chemisorption can greatly differ, depending on the chemical identity and the surface structural properties. The bond between the adsorbate and adsorbent in chemisorption is either ionic or covalent.

Chemisorption (chemical absorption) processes are characterized by a high capability of absorbing large amounts of acid gases. They use a solution of a relatively weak base, such as monoethanolamine. The acid gas forms a weak bond with the base which can be regenerated easily. Mono- and diethanolamine derivatives are frequently used for this purpose. The amine concentration normally ranges between 15 and 30%. The gas stream is passed through the amine solution where sulfides, carbonates, and bicarbonates are formed. Diethanolamine is a favored absorbent due to its lower corrosion rate, smaller amine loss potential, fewer utility requirements, and minimal reclaiming needs. Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS), while monoethanolamine reacts irreversibly with 95% of the carbonyl sulfide and forms a degradation product that must be disposed in an environmentally acceptable manner.

In contrast with chemisorption is physisorption which leaves the chemical species of the adsorbate and surface intact. It is conventionally accepted that the energetic threshold separating the binding energy of physisorption from that of chemisorption is approximately 0.5 eV per adsorbed species.

See also: Absorption, Adsorption, Physisorption.

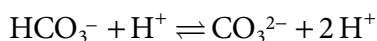
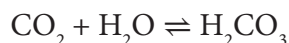
Chemistry in the Aquasphere

The composition and chemistry of the aquasphere are of importance for several reasons, but primarily because of the interactions between the aquasphere and living organisms. However, chemistry in the water systems of the Earth (oceans, rivers, streams, and lakes) are not as straightforward as it may seem but, in many cases, aqueous life has had to adapt to the chemistry. In addition, the impact of human activity on the chemistry of the water systems has increased over time, with pollution from various practices significantly affecting the water systems.

The water cycle offers a description of the means by which water evaporates from the surface of the Earth, rises into the atmosphere, cools, condenses to form clouds, and falls again to the surface as precipitation. This system of the cycling of water is intimately linked with energy exchanges among the atmosphere, the ocean, and land that determine the climate of the Earth and cause much of natural climate variability. For example, approximately 75% of the energy (or heat) in the global atmosphere is transferred through the evaporation of water from the surface of the Earth. On land, water evaporates from the ground, mainly from soils, plants (through transpiration), lakes, and streams. In fact, approximately 15% v/v of the water entering the atmosphere is from evaporation from the land surfaces and evapotranspiration from plants which (i) cools the surface of the Earth, (ii) cools the lower atmosphere, and (iii) provides water to the atmosphere to form clouds.

The major chemical and physical components of the global water cycle include (i) the evaporation from the ocean and land surfaces, (ii) the transport of water vapor by the atmosphere and precipitation onto the ocean and land surfaces, (iii) the net atmospheric transport of water from land areas to ocean, and (iv) the return flow of fresh water from the land back into the ocean. The additional components of oceanic water transport are few, including the mixing of fresh water through the oceanic boundary layer, transport by ocean currents, and sea ice processes.

Other than the illegal dumping of chemicals in various water systems, a major chemical effect is the acidification of the water systems of the Earth, particularly the acidification of the oceans which is manifested by is the ongoing decrease in the pH of the oceans caused by the uptake of carbon dioxide (CO_2) from the atmosphere. Seawater is slightly basic ($\text{pH} > 7$), and ocean acidification involves a shift toward pH-neutral conditions rather than a transition to acidic conditions ($\text{pH} < 7$). Thus, dissolving carbon dioxide in water increases the hydrogen ion (H^+) concentration in the water, and thus decreases the pH of the water:



Changes in water chemistry can have extensive direct and indirect effects on organisms and the habitats of the organisms. One of the most important repercussions of increasing ocean acidity relates to the production of shells and plates out of calcium carbonate (CaCO_3). This process (calcification) is important to the biology and survival of a wide range of aqueous organisms and involves the precipitation of dissolved ions into solid calcium carbonate structures which are vulnerable to dissolution unless the surrounding water contains saturating concentrations of carbonate ions (CO_3^{2-}).

The saturation state (Ω) of seawater for a mineral is a measure of the thermodynamic potential for the mineral to form or to dissolve, and for calcium carbonate is described by the following equation:

$$\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}$$

As represented by this equation, Ω is the product of the concentrations of the reacting ions that form the mineral (Ca^{2+} and CO_3^{2-}), divided by the product of the concentrations of those ions when the mineral is at equilibrium (K_{sp}), that is, when the mineral is neither forming nor dissolving.

Using seater as an example, a natural horizontal boundary is formed as a result of temperature, pressure, and depth (the saturation horizon). Above this saturation horizon, Ω has a value greater than 1, and CaCO_3 does not readily dissolve. Below this depth, Ω has a value less than 1, and calcium carbonate will dissolve. However, if its production rate is high enough to offset dissolution, calcium carbonate can still occur where Ω is less than 1. The carbonate compression depth occurs at the depth in the ocean where production is exceeded by dissolution.

See also: Aquasphere.

Chemistry in the Atmosphere

The composition and chemistry of the atmosphere of the Earth is of importance for several reasons, but primarily because of the interactions between the atmosphere and living organisms. The chemistry that occurs in the atmosphere involves the chemical processes that occur in the gas and particle phases to better predict their impact on air pollution and global climate change. Gases and particles are emitted to the atmosphere, often as pollutants, and they may undergo a wide range of chemical processes because of the occurrence of a variety of chemical constituents in the atmosphere. In fact, atmospheric chemistry plays an important role in controlling climate change. As an example, aerosol particles impact climate through direct radiative forcing, by indirectly modifying clouds, and by modifying carbon uptake.

The atmosphere is the envelope of gases surrounding the Earth, and it is subdivided into regions depending on the altitude. The constituents of the atmosphere are primarily nitrogen (N_2 , 78.08% v/v), oxygen (O_2 , 20.95% w/w), and water vapor (0 to 0.25% w/w), although the concentration of water vapor (H_2O) is highly variable, especially near the surface, where volume fractions can be as high as 4% in the tropics. There are many minor constituents or trace gases such as (alphabetically rather than by abundance, which is variable) argon (Ar), carbon dioxide (CO_2), helium (He), hydrogen (H_2), krypton (Kr), methane (CH_4), neon (Ne), nitrous oxide (N_2O), ozone (O_3), and water vapor (H_2O) (Table C-6).

Table C-6 Approximate composition of the atmosphere.

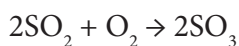
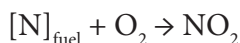
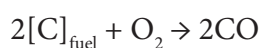
Component, % v/v	Amount, % v/v
Major components:	
Nitrogen (N_2)	78.08
Oxygen (O_2)	20.95
Minor/trace components:	
Argon (Ar)	0.93
Water vapor (H_2O)	0.025*
Carbon dioxide (CO_2)	0.035
Neon (Ne)	0.018
Helium (He)	0.00052
Methane (CH_4)	0.00014
Krypton (Kr)	0.00010
Nitrous oxide (N_2O)	0.00005
Hydrogen (H_2)	0.00005
Ozone (O_3)	0.0000007

*Variable; can be as high as 4% v/v in humid areas.

In addition to the gaseous constituents, the atmosphere also contains suspended solid and liquid particles. Aerosols are particulate matter usually less than 1 micron in diameter (also called 1 micrometer which is equivalent to $1 \text{ meter} \times 10^{-6}$ in diameter, i.e., one millionth of a meter or one thousandth of a millimeter, 0.001 mm, or approximately 0.000039 of an inch) that are created by gas-to-particle reactions and are lifted from the surface by the winds. A portion of these aerosols can become centers of condensation or deposition in the growth of water and ice clouds. Cloud droplets and ice crystals are made primarily of water with some trace amounts of particles and dissolved gases. Their diameters range up to 100 micrometers. Water or ice particles larger than approximately 100 microns begin to fall because of gravity and may result in precipitation at the surface.

There are a number of critical chemistry issues that are associated with a changing atmosphere, including photochemical smog, global climate change, toxic air pollutants, acidic deposition, and stratospheric ozone depletion. Much of the anthropogenic (human) impact on the atmosphere is associated with the increasing use of fossil fuels as an energy source – for things such as heating, transportation, and electric power production. Photochemical smog/tropospheric ozone is a serious environmental problem that has been associated with burning such fuels, and the result has been the formation and deposition of acid rain.

Acid rain is formed when sulfur oxides and nitrogen oxides react with water vapor and other chemicals in the presence of sunlight to form various acidic compounds in the atmosphere. The principle source of acid rain-causing pollutants, sulfur oxides and nitrogen oxides, is from fuel combustion – specifically from fuels that contain sulfur and nitrogen:



sulfurous acid



sulfuric acid



nitrous acid



nitric acid

Two of the pollutants that are emitted are hydrocarbon derivatives (e.g., unburned fuel) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight

in which the NO is converted to nitrogen dioxide (NO_2) – a brown gas and at sufficiently high levels can contribute to urban haze. However, a more serious problem is that nitrogen dioxide (NO_2) can absorb sunlight and break apart to produce oxygen atoms that combine with the oxygen in the air to produce ozone (O_3), a powerful oxidizing agent, and a toxic gas.

See also: Atmosphere.

Chemistry in the Geosphere

The geosphere (also called the land systems) constitutes the terrestrial component of the systems of the Earth and encompasses all processes and activities related to the human use of land, including, technological and organizational investments and arrangements, as well as the benefits gained from land and the unintended social and ecological outcomes of societal activities. Changes in land systems have large consequences for the local environment and human well-being and are at the same time pervasive factors of global environmental change. In more specific terms, the lithosphere refers to the minerals in the crust of the Earth whereas the term geosphere is often more broad in coverage and refers to the complex and variable mixture of minerals, organic matter, water, and air which make up the soil.

Chemistry in the geosphere is related to the chemistry of the atmosphere and the aquasphere. In the relationships between the atmosphere, the water systems, and the land systems, acid rain is the precipitation phenomena that incorporate anthropogenic acids (i.e., those acids which are the result of human activities) and other acidic materials. The deposition of acidic materials into the water systems and onto the land occurs in both wet and dry forms as rain, snow, fog, dry particles, and gases. The effect of acid rain (acid deposition) on a particular ecosystem depends largely on the sensitivity of the ecosystem to the acid deposition. There is also the ability of the ecosystem to neutralize the acid as well as the concentration and composition of acid reaction products and the amount of acid added to the system.

Trace element is a term that refers to those elements that occur at low levels in a given system. There are a variety of trace elements encountered in natural waters, some of which are the nutrients required for animal and plant life. Of these, many are essential at low levels but toxic at higher levels. This is typical for many substances in the aquatic environment, a point that must be kept in mind in judging whether a particular element is beneficial or detrimental. Some of these elements, such as lead or mercury, have such toxicological and environmental significance that they are discussed in detail in separate sections.

Some of the heavy metals are among the most harmful of the elemental pollutants. These metals include essential elements like iron as well as toxic metals like lead (Pb), cadmium (Cd), and mercury (Hg). Most of them have a tremendous affinity for sulfur and attack sulfur bonds in enzymes, thus immobilizing the enzymes. Protein carboxylic acid ($-\text{COOH}$) derivatives and amino ($-\text{NH}_2$) groups are also chemically bound by heavy metals. Cadmium, copper, lead, and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate compounds or catalyze their decomposition.

More specifically, the chemistry that occurs in soils is a major driver of the chemistry in the geosphere. Soils transport and move water, provide homes for thousands of bacteria and other creatures, and have many different arrangements of weathered rock and minerals. When soils and minerals weather over time, the chemical composition of soil also changes.

Ion exchange involves the movement of cations (positively charged elements like calcium, magnesium, and sodium) and anions (negatively charged elements such as chloride, and compounds such as like nitrate) through the soils. In the United States, cation exchange is much more common. On the other hand, anion exchange is the interchange between a cation in the solution of water around the soil particle, and another cation that is stuck to the clay surface. The number of cations in the soil water solution is much smaller than the number that is attached to soil particles.

The total amount of positive charges that the soil can absorb (the cation exchange capacity) impacts the speed that nutrients move through the soil profile. A soil with a low cation exchange capacity is much less fertile because it cannot hold on to many nutrients, and they usually contain less clays. If the soil has a low cation exchange capacity,

it is important to apply fertilizer in small doses so it does not infiltrate into the groundwater. Also, soil with a low cation exchange capacity is less able to hold spilt chemicals.

The soil pH is a measure of soil acidity or alkalinity. The pH can range from 1 to 14, with values 0-7 being acidic, and 7-14 being alkaline – soils usually range from 4 to 10. The pH is one of the most important properties involved in plant growth, as well as understanding how rapidly reactions occur in the soil. For example, the element iron becomes less available to plants at a higher pH, which can create iron deficiency. Crops usually prefer a pH on the order of 5.5 to 8, but the value depends on the crop.

Soil particles have the ability to capture different nutrients and ions (the process is known as sorption) in which one substance takes up or holds another. In this case, soils that have high sorption can retain environmental contaminants on the particles. Soil precipitation occurs during chemical reactions when a nutrient or chemical in the soil solution (water around soil particles) transforms into a solid which is an important aspect of soils that are salty.

Interactions occur between the soil and the organic matter in the soil – the organic matter is the material derived from the decay of plants and animals which contains many hydrogen and carbon compounds. The arrangement and formation of these compounds influence a soil's ability to handle spilt chemicals and other pollutants.

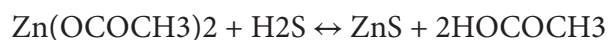
Soils that alternate between wet and dry range from aerobic (having high amounts of oxygen) to anaerobic (low amounts of oxygen) which determines how soils chemically react. Oxidation and reduction reactions occur continuously.

See also: Geosphere.

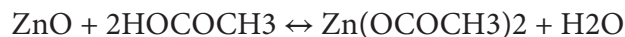
Chemsweet Process

The Chemsweet process is a batch process for the removal of hydrogen sulfide from gas streams. The chemicals used are a mixture of zinc oxide, zinc acetate, water, and a dispersant to keep the zinc oxide particles in suspension. When one part is mixed with five parts of water, the acetate dissolves and provides a controlled source of zinc ions that react instantaneously with the bisulfide and sulfide ions that are formed when hydrogen sulfide dissolves in water. The zinc oxide replenishes the zinc acetate:

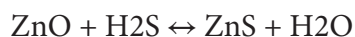
Sweetening:



Regeneration:



Overall:



The presence of carbon dioxide in the gas stream is of little consequence as the pH of the slurry is low enough to prevent significant absorption of carbon dioxide, even when the ratio of CO₂ to H₂S is high.

The Chemsweet process can treat gas streams with a high hydrogen sulfide concentration and has been operated between pressures of 89 and 1415 psi. Mercaptan concentrations in excess of 10% of the hydrogen sulfide concentration in the gas stream can be a problem. Some of the mercaptans will react with the zinc oxide and be removed from the gas. The resulting zinc mercaptide forms a sludge and possibly cause foaming problems.

However, the process uses dispersants, and antifoam additives to stabilize the process. In addition, the spent media can be disposed of in an industrial landfill only after passing leachate tests. If the leachate contains more than 20 ppm of zinc and zinc compounds, then it must be treated as a hazardous waste.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Chinese Tallow Tree

The Chinese tallow tree (*Triadica sebifera*) is a plant native to central China. The tree is most favorably grown in warm climates with well-drained soils, with the fruit being harvested in early winter after the leaves have fallen off. The Chinese Tallow Tree is shade, sun, drought, flood, freeze, and salt-tolerant, making it a plant that is hard to control. One seed contains approximately 20% w/w oil, 24% w/w tallow, 11% w/w extracted protein, 8% w/w fibrous coat, and 37% w/w shell. The tree is a member of family that has many poisonous plants, and the seed kernel oil (as opposed to the waxy outer coating around the seed) is toxic indicating a reason for caution when the tree is (or the seeds are) harvested for use.

The tree has been cultivated as a seed-oil crop in China for at least 14 centuries. Candles, soap, cloth dressing, and fuel are made from the tallow. Chinese vegetable tallow is a solid fat that is in the outer covering of the Chinese tallow seeds. The kernels produce an oil (called stillingia oil) that is used in machine oils, as a crude lamp oil, and in making varnishes and paints. It can also be converted to charcoal, methanol, ethanol, and potentially, the oil from the seeds can be a substitute for crude oil.

The oil keeps well and probably does not need refining. Since the Chinese Tallow Tree is hard to control, making it seem as if there are no impediments to its growth and often giving it the title of an invasive species in many states, California uses the tree as a street and ornamental plant and it does not interfere with the other plant life. With some tolerance to salinity, the tallow trees could be investigated as energy crops for saline situations. The tree has the ability to reach reproductive age in as little as 3 years and to remain productive for at least 60 years. It does not seem to have a preference for disturbed areas over undisturbed areas and can grow in a variety of places, including both full sunlight and shade.

Circulating Fluidized Bed Gasifier

In a circulating fluid bed (CFB) gasifier, the turbulent bed solids are collected, separated from the gas, and returned to the bed, forming a solids circulation loop. The circulating fluidized bed can be differentiated from a bubbling fluidized bed in that there is no distinct separation between the dense solids zone and the dilute solids zone. Lower bed density can be achieved with increase in gas flow rates in excess of transport velocity of the fluidized bed particles. The residence time of the solids in the circulating fluid bed is determined by the solids circulation rate, attrition of the solids, and the collection efficiency of the solids in the cyclones.

The advantages of the circulating fluidized bed gasifiers are that they are (i) suitable for rapid reactions, (ii) high conversion rates possible with low tar and unconverted carbon, and (iii) high heat transport rates possible due to high heat capacity of bed material.

The disadvantages are (i) temperature gradients occur in the direction of the solid flow, (ii) the size of fuel particles required to determine minimum transport velocity, and (iii) high velocities may result in equipment erosion and heat exchange less efficient than bubbling fluidized bed.

See also: Gasification, Gasification of Biomass, Gasification of Biomass – Feedstock Preparation.

Claus Process

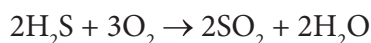
The Claus sulfur recovery process is the most widely used technology for recovering elemental sulfur from sulfur-containing (sour) gas streams. Most of the world's sulfur is produced from the acid gases coming from gas treating. Conventional three-stage Claus plants can approach 98% sulfur recovery efficiency. However, since environmental regulations have become stricter, sulfur recovery plants are required to recover sulfur with over 99.8% efficiency. To meet these stricter regulations, the Claus process underwent various modifications and add-ons.

The add-on modifications to the Claus plant can be considered as a separate operation from the Claus process, in which case it is often called a tail gas treating process. Other sulfur recovery processes can replace the Claus process where it is uneconomic or cannot meet the required specifications. Usually, such processes are used in small-scale

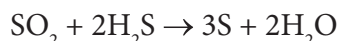
plants, or where the hydrogen sulfide content of the acid gas is too low for a Claus plant or one of its modified versions.

The chemistry of the Claus process involves partial oxidation of hydrogen sulfide to sulfur dioxide and the catalytically promoted reaction of hydrogen sulfide and sulfur dioxide to produce elemental sulfur. The reactions are staged and are as follows:

Thermal stage:



Thermal and catalytic stage:



The first stage of the process converts hydrogen sulfide to sulfur dioxide and to sulfur by burning the acid-gas stream with air in the reaction furnace. This stage provides sulfur dioxide for the next catalytic phase of the reaction. Multiple catalytic stages are provided to achieve a more complete conversion of the hydrogen sulfide. Each catalytic stage consists of a gas reheater, a reactor, and a condenser. Condensers are provided after each stage to condense the sulfur vapor and separate it from the main stream. Conversion efficiencies of 94-95% can be attained with two catalytic stages, while up to 97% conversion can be attained with three catalytic stages. The effluent gas is incinerated or sent to another treating unit for tail-gas treating before it is exhausted to atmosphere.

The sulfur recovery by the Claus process depends upon such things as (i) the composition of the gas stream, (ii) the age of the catalyst, and (iii) the number of reactor stages. Typical sulfur recovery efficiencies for Claus plants are 90% to 96% for a two-stage plant and 95% to 98% for a three-stage plant. Because of equilibrium limitations and other sulfur losses, overall sulfur recovery efficiency in a Claus unit usually does not exceed 98%.

The off-gas leaving a Claus plant is referred to as tail gas and, in the past, was burned to convert the unreacted hydrogen sulfide to sulfur dioxide, before discharge to the atmosphere, which has a much higher toxic limit. However, the increasing standards of efficiency required by the pressure from environmental protection have led to the development of a large number of Claus tail gas clean-up units, based on different concepts, in order to remove the last remaining sulfur species.

The oxygen-blown Claus process was originally developed to increase capacity at existing conventional Claus plants and to increase the flame temperatures of gases having low hydrogen sulfide content. The process has also been used to provide the capacity and operating flexibility for sulfur plants where the feedstock gas stream is variable in flow and composition such as often found in refineries.

The SuperClaus process consists of a thermal stage followed by three or four catalytic reaction stages with sulfur removed between stages by condensers. The first two or three reactors are filled with standard Claus catalyst, while the last reactor is filled with the selective oxidation catalyst. In the thermal stage, the acid gas is burned with a less-than-stoichiometric amount of controlled combustion air so that the tail gas leaving the last Claus reactor typically contains 0.5 to 0.9 vol.% of hydrogen sulfide. There are two main principles applied in operating the SuperClaus process: (i) operating the Claus plant with excess hydrogen sulfide to suppress the sulfur dioxide content in the Claus tail gas, and (ii) selective oxidation of the remaining hydrogen sulfide by the process catalyst selectively converts the hydrogen sulfide in the presence of water vapor and excess oxygen to elemental sulfur.

In the Clauspol process, the Claus tail gas is contacted counter-currently with an organic solvent in a low pressure drop packed column. Hydrogen sulfide and sulfur dioxide are absorbed in the solvent and react to form liquid elemental sulfur according to the Claus reaction, which is promoted by an inexpensive dissolved catalyst. The solvent is pumped around the contactor, and the heat of reaction is removed through a heat exchanger to maintain a constant temperature above the sulfur melting point. Due to the limited solubility of sulfur in the solvent, pure liquid sulfur separates from the solvent and is recovered from settling section at the bottom of the contactor. This process allows sulfur recovery up to 99.8%, and the recovery level can be customized by adapting the size of the contactor.

See also: Gas Cleaning, Gas Processing, Gas Treating, Tail Gas Cleaning.

Clay Minerals

The term *clay* is a type of fine-grained natural soil material that contains hydrous aluminum phyllosilicates (which are the actual clay minerals) that develop plasticity when wet. Geologic clay deposits are mostly composed of phyllosilicate minerals containing variable amounts of water trapped in the mineral structure. Clays are plastic due to particle size and geometry as well as water content, and become hard, brittle, and non-plastic upon drying or firing. Depending on the soil content in which the clay exists, clay can appear in various colors from white to dull gray or brown to deep orange-red. On the other hand, clay minerals (often simply referred to, and some investigators would state incorrectly, as *clays*) are silicate minerals, which usually contain aluminum also, and constitute one of the most significant classes of secondary minerals. Although many naturally occurring deposits include both silts and clay minerals, the latter (the clay minerals) is distinguished from other fine-grained soils by differences in size and mineralogy (Table C-7).

Table C-7: General groups of clay minerals.

Group	Description
Kaolin	Includes kaolinite, halloysite minerals, and nacrite.
	Polymorphs of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})$.
Smectite	Includes dioctahedral smectites such as montmorillonite, nontonite, beidellite, and trioctahedral smectites such as saponite.
Illite	Includes the clay-micas; illite is the only common mineral.
Chlorite	Includes a wide variety of similar minerals with considerable chemical variation.
Others	Includes palygorskite (also known as attapulgite and sometimes referred to as Attapulgius clay) and sepiolite.
	Clay minerals with long water channels internal to their structure.

Silt, which is a fine-grained soil that does not include clay minerals, tends to have larger particle sizes than clay minerals (Table C-8).

Table C-8 Approximate sizes of the various rock types.

Name	Diameter (millimeters)
Boulder	>256
Cobble	64 to 256
Pebble	2 to 64
Sand	1/6 to 2
Silt	1/256 to 1/6
Clay	<1/256

More specifically, clay minerals are hydrous aluminum phyllosilicate derivatives that often contain variable amounts of (alphabetically rather than by abundance) alkaline earth metals (any of the six chemical elements that comprise Group IIa of the periodic table – beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), alkali metals iron, magnesium, as well as other cations. Clay minerals form in the presence of water and have been important to life, and many theories of abiogenesis involve clay minerals (Hillier, 1995). They are important constituents of soil, and have been useful to humans since ancient times in agriculture and manufacturing.

Weathering of rocks and soil is the primary way that clays and clay minerals form at the surface of the Earth. The weathering process involves physical disaggregation and chemical decomposition that change original minerals to

clay minerals; weathering is uneven, and many stages of breakdown may be found in the same clay sample. Factors governing rock weathering and soil formation include the initial type of rock, the ratio of water to rock, the temperature, the presence of organisms and organic material, and the amount of time. The types of clay minerals found in weathering rocks strongly control how the weathered rock behaves under various climatic conditions (such as humid-tropical, dry-tropical, and temperate conditions).

Kaolinite is found in most weathering zones and soil profiles. Montmorillonites, which are chemically more complex than kaolinites, are common in the lower parts of weathering profiles, nearer the rock, where chemistry exerts a strong control on mineralogy. Complex mixed-layer clay minerals (such as illite-smectites) are abundant in clay assemblages that develop from mica-bearing precursor rocks, such as the granite plutons that occur in temperate regions of the Northeastern United States. For example, a large component of soils formed by weathering of granites may consist of metastable muscovite, biotite, and chlorite. These minerals will alter progressively to clay minerals.

Clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. Most clay minerals form where rocks are in contact with water, air, or steam. Examples of these situations include weathering boulders on a hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water, and rocks in contact with water heated by magma (molten rock). All of these environments may cause the formation of clay minerals from preexisting minerals. Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits that are of economic interest (for example, bentonite, primarily montmorillonite used for drilling muds and clays used in ceramics).

Clay minerals typically form over long periods as a result of the gradual chemical weathering of rocks over a period of hundreds of years, usually silicate-bearing, by low concentrations of, for example, carbonic acid (H_2CO_3). This acidic chemical usually migrates through the weathering rock after leaching through upper weathered layers. In addition to the weathering process, some clay minerals are formed through hydrothermal activity. Clay deposits are typically associated with low energy deposition environments such as large lakes and marine basins. In addition, there are two types of clay deposits: (i) primary deposits and (ii) secondary deposits. In the former deposits (primary deposits), the clays (frequently referred to as primary clays) have been formed as residual deposits in the soil and remain at the site of formation, while in the latter deposits (secondary deposits), the clays (frequently referred to as secondary clays) are clays that have been transported from their original location by water erosion and deposited in new sedimentary deposits.

Clay Treating Process

Treating process distillates by passing the distillate through materials possessing decolorizing power has been in operation for many years. For example, various clay minerals and similar materials are used to treat crude oil fractions to remove diolefins, asphaltic materials, resins, acids, and constituents that give rise to color. Distillates from pyrolysis processes can be clay-treated to remove diolefins that formed gums in liquid fuels. Other processes have now largely superseded this use of clay treatment, in particular by the use of inhibitors, which, added in small amounts to liquid fuels, prevent gums from forming.

The original method of clay treatment was to percolate a liquid fuel through a tower containing coarse clay pellets. As the clay absorbed impurities from the fuel, the clay became less effective and the clay removed from the adsorption tower periodically restored the activity of the clay and burning the absorbed material under carefully controlled conditions so as not to sinter the clay.

See also: Clay Minerals.

Climate Change

By definition, climate change is a long-term shift in weather conditions that is identified by changes in temperature, precipitation, winds, and other indicators which can involve both changes in average conditions and changes in variability, including, for example, extreme events. The physical climate system involves the atmosphere, land surfaces,

and oceans of the Earth, along with the snow and ice that are so prominent in many northern climes. These components interact with one another and with aspects of the biosphere of the Earth to determine not only the day-to-day weather, but also the long-term averages that are referred to as *climate*.

The most general definition of *climate change* is a change in the statistical properties of the climate system when considered over long periods of time, regardless of cause. Accordingly, fluctuations over periods shorter than a few decades, such as El Niño, do not represent climate change. The term is sometimes used to refer to climate change caused by human activity, as opposed to changes in climate that may have resulted as part of the natural processes of the Earth. In this sense, especially in the context of environmental policy, the term *climate change* has unfortunately and incorrectly been associated with anthropogenic (human activities) global warming as the causative factor. Within scientific journals, *global warming* refers to an increase in the surface temperature of the Earth while *climate change* is an all-inclusive term that includes global events.

The issue of global climate change is often associated with the use of fossil fuels as sources of energy. Of most concern is the increase in emissions of carbon dioxide (CO₂) due to emissions from fossil fuel combustion. Other factors, including land use, ozone depletion, animal agriculture, and deforestation, are also of concern in the roles they play – both separately and collectively – in affecting climate, microclimate, and various climate variables.

Climate change is inevitable and is already happening as a result of the current interglacial period. Contributing to this change are (i) natural effects, which include the Earth in an interglacial period and (ii) anthropogenic effects, which include the release of non-indigenous gases into the atmospheres. However, the exact contribution of each to global climate change is unknown and the blame can only be partially laid on the shoulders of interglacial period and somewhat less on anthropogenic effects.

Evidence for a significant change in the climate is substantial, but – and perhaps more interestingly – the specific reasons for this change are not fully understood, although reasonably complete global records of surface temperature are available beginning from the mid-late 19th century – the time period after the Little Ice Age when warming was occurring. In the late decades of the 20th century, the term *global warming* was in vogue and substantial government funding was available for research in this area. Within the recent decades, the cause of *global cooling* has been diminished and the term *global warming* took over. But this term did not fit the prevalent weather patterns, and it is now the cause of *global climate change* – a more convenient umbrella-like catch-all for any changes (warming or cooling) that are the result of cyclic weather patterns.

In reality, the climate of the Earth can be affected by natural factors that are external to the climate system, such as changes in volcanic activity, solar output, and the variance of the orbit of the Earth around the Sun. Of these, the two factors relevant on timescales of contemporary climate change are changes in volcanic activity and changes in solar radiation. In terms of the energy balance of the Earth, these factors primarily influence the amount of incoming energy. Volcanic eruptions are episodic and have relatively short-term effects on climate.

Moreover, there are indications of a Medieval Warming Period in which the climate was warm, or warmer than it is currently. Such a statement is more than a mere scientific curiosity and has wide significance. It is generally believed that the causative agent of the global climate change is the increased amounts of carbon dioxide in the atmosphere as compared to hundreds of years ago. The carbon dioxide is produced through the combustion of fossil fuels, and the amount in the atmosphere of times past has been deduced by determination of the amounts of carbon dioxide in ice cores. But salient facts related to the mobility of carbon dioxide in ice and snow are ignored. In addition, the temperatures of the Earth during the Medieval Warm Period could not have been due to fossil fuel consumption, and therefore, it is more than likely that this demonstrates that the warming of the earth that was initiated during the last century may have been just another natural fluctuation.

A crucial feature of the climate system is that the energy of the Sun is not distributed uniformly, but is rather most intense at the equator and weakest at the poles. This non-uniform energy distribution leads to temperature differences, which the atmosphere and ocean act to reduce by transporting heat from the warm tropics to the cold Polar Regions. This non-uniform heating and the resulting heat transport give rise to ocean currents, atmospheric circulation, evaporation, and precipitation that are ultimately experienced as weather.

Since there is little or nothing that can be done to deter climate change because of the current interglacial period when warming will occur and because there is currently no major alternative to fossil fuels, politicians and other leaders, who clearly know better, feel compelled to deny it. For exactly the same reasons, politicians do not acknowledge

the needs for preparing for peak energy – perhaps it is too far into the future that peak energy will occur, and for many politicians, looking to the future means looking to the time of the next election.

Currently, in the context of climate change, there needs to be a lesser reliance on emotion and more reliance on hard accurate and reliably unbiased science. On the other hand, publicly singling out specific researchers on any side of the discussion based on perspectives that they have expressed sends a dangerous message to all researchers.

Climate change is more of a natural hazard and arises as part of the evolution of the Earth, and the idea that there can be a one-size-fits-all global solution to address future climate change fails to deal with the real and major issue of climate and climate-related issues. There should be planning (rather than responding to the panic-laden issue related to carbon dioxide) as to the means by which future generations will deal with the effects of an interglacial period on the Earth. There is a need to uphold the principles of fair-minded examination of the evidence and allow open debate.

In spite of the emphasis on increased amounts of carbon dioxide in the atmosphere being the cause of climate change, there are several other factors that can influence the climate which have been largely ignored in favor of the carbon dioxide theory. Moreover, it is the recognition of these events that will eventually stabilize global climate change which can be widely applied to reorient policies and scientific strategies for various countries. In fact, the current information for global climate change points to global warming/climate change being influenced by the sum of all effects with no one effect (such as the anthropogenic effect) being the major contributor from a multi-component group of effects.

The Earth is constantly changing since its formation and has gone through different eras like glaciations, among others. However, these changes need thousands of years to be made visible, and the current increase in the average temperature of the Earth since the pre-industrial period is happening – provided that the measurements of past climatic temperatures are accurate and beyond reproach. Thus, the assessment that the warming trend that has occurred (somewhat erratically) over the past 100 years is very likely to have some origins in natural events – the precise contributions of natural effects and anthropogenic effects on the climate are not known, but it is more accurate to conclude that many factors continue to influence climate and whether or not human activities have become a dominant force, and are responsible for most of the warming observed, is still very much open to question.

See also: Global Climate Change.

Closed-Loop Biomass

Closed-loop biomass is any organic matter from a plant which is planted for the exclusive purpose of being used to produce energy.

The term includes crops grown, in a sustainable manner, for the purpose of optimizing their value for bioenergy and bioproduct uses. This includes annual crops such as maize and wheat, and perennial crops such as trees, shrubs, and grasses such as switch grass. However, the term does not include wood or agricultural wastes or standing timber nor does it include biomass burned in conjunction with fossil fuel (co-firing) beyond such fossil fuel required for startup and flame stabilization.

A closed-loop biomass energy system includes at least one agricultural facility that produces agricultural waste: a waste processing system operable to convert the waste into biomass. It is also a wastewater treatment system operable to treat wastewater created by the waste processing system and an energy production system operable to utilize the biomass to produce energy and provide the energy to an energy end-user.

See also: Biomass.

Coagulation

Coagulation is the term usually applied to the neutralization of surface charges on particles of colloidal or near colloidal size. These charges are of the same sign for all the particles in a given suspension and can be either positive or negative. Thus, they repel each other and hold the particles apart thereby preventing agglomeration. Destroying the

repulsions between particles by neutralizing the charges that stabilize the suspension allows the particles to approach each other closely enough to touch. They can then collect into larger aggregates which can settle effectively.

The additives that are effective for neutralizing surface charge on solid particles are highly ionic electrolytes, preferably containing ions of multiple charge. The effectiveness of trivalent ions is 10 to 100 times that of monovalent or divalent ions, as measured by coagulation time. Typical coagulation additives are acids, lime (calcium hydroxide), alum [aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$], and ferric chloride (FeCl_3) or ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$]. The additive is mixed into the wastewater with intense mixing to distribute it rapidly throughout the feed stream. This is in direct contrast with flocculation, which is enhanced by gentle mixing.

See also: Chemical Precipitation, Flocculation, Sedimentation.

Coarse Materials

The coarse material, referring to biomass, includes wood residues suitable for chipping, such as slabs, edgings, and trimmings.

See also: Biomass.

Co-Combustion

Co-combustion is the combustion of one feedstock with another and is often used as a means of disposal of waste materials.

The co-combustion of waste such as scrap tires and tire-derived fuels is another option for removal of the backlog of scrap tires in storage ready for waste disposal.

Tire rubber can be combusted together with other fossil fuels as well as biomass without the major alteration of an existing combustion facility. Energy generation using scrap tires and tire-derived fuels as a supplemental fuel to coal is of particular interest and is being practiced throughout the world.

The rationale behind the use of tire rubber as a supplemental fuel for power generation is based on the following: (i) excellent combustion characteristics and high heating value, (ii) lower cost and good availability, (iii) relatively low sulfur content, especially on a btu basis, and (iv) reducing the environmental burden and health effects of tire stock piles. The heating value of tires is on the order of 15,000 to 16,000 Btu/lb, whereas typical bituminous coal (washed) has a heating value of 12,000 to 13,000 Btu/lb. Typically, the sulfur content of scrap tires and tire-derived fuels is 1.5-2%. Considering the sulfur dioxide (SO_2) emission potential and the generated energy value of the fuel (pound SO_2 produced per million BTU generated), the result is closer to that for low-sulfur containing coals.

However, the co-combustion of tire and tire-derived fuel may alter the emission characteristics of the combustion facility. The environmental impacts and health effects of tire co-combustion need to be carefully assessed for each plant with all relevant factors taken into account, viz., the combustion process itself, combustion conditions, plant design, control equipment, and its efficiency with respect to specific trace elements, feed material properties, blend ratios, and analysis techniques.

See also: Combustion, Tires – Scrap.

COED/COGAS Process

The COED/COGAS process involves the flow of carbonaceous feedstock (usually coal) through four fluidized bed pyrolysis stages, each operating at a higher temperature than the preceding unit. When coal is employed as the feedstock, the temperatures of the stages are selected to be just below the maximum temperature to which the particular feed coal can be heated without agglomerating.

Typical operating temperatures are 315 to 345°C (600 to 650°F) in the first stage, 425 to 455°C (800 to 850°F) in the second stage, 540°C (1,000°F) in the third stage, and 870°C (1,600°F) in the fourth stage. However, the optimum

stage temperatures (and even the number of stages) vary depending on the properties of the feed coal and therefore on the properties of the biomass feedstock.

Heat for the process is provided by burning a portion of the product char with oxygen in the presence of steam in the fourth stage. Hot gases from this stage flow countercurrent to the char and provide the hot fluidizing medium for the intermediate pyrolysis stages. The gases leaving both the first and second stages are passed to cyclones which remove the fines, but the vapors leaving the cyclones need to be quenched in a Venturi scrubber to condense the oil, and the gases and oil are separated in a decanter. The gas is desulfurized and then steam-reformed to yield hydrogen and fuel gas; the hydrogen is returned to the process.

The oil from the decanter is dehydrated, filtered, and hydrotreated to remove nitrogen, sulfur, and oxygen (forming ammonia, hydrogen sulfide, and water, respectively) to produce a heavy synthetic crude oil (ca. 25° API). The char produced by the process is desulfurized in a shift kiln, where hydrogen is treated with the char to produce hydrogen sulfide which is then absorbed by an acceptor, such as limestone or dolomite.

The COGAS process involves the gasification of the COED char to produce a synthesis gas composed of carbon monoxide and hydrogen. The heat for the char gasification reaction is provided by the combustion of part of the char.

See also: Gasification, Gasification of Biomass.

Co-Firing

Co-firing refers to the practice of introducing biomass as a supplementary energy source in coal plants. It is a near-term, low-cost option for using woody residue. Co-firing results in a net reduction in greenhouse gases and lower emissions of sulfur dioxide and nitrogen oxides.

Biomass co-firing involves the addition of biomass as a partial substitute fuel in high efficiency coal boilers. In the process, coal and biomass are co-combusted in boilers that have been designed to burn coal. For this purpose, the existing coal power plant has to be partly reconstructed and retrofitted. Co-firing is an option to convert biomass to electricity, in an efficient and clean way, and to reduce greenhouse gas emissions of the power plant.

Over the past three decades, the process of co-firing has seen a rapid development. Many plants have been retrofitted for demonstration purposes and others have been newly built to allow for biomass co-firing. There are three different concepts for co-firing biomass in coal boilers, and these concepts are (i) direct co-firing, (ii) indirect co-firing, and (iii) parallel co-firing.

In the direct co-firing option, the biomass and the coal are combusted in the same furnace. The mills for the grinding of the fuel and the burners may be separate. This depends on the biomass used and its fuel properties. This concept is most commonly used because it is the easiest to implement and the most cost-effective.

The indirect co-firing concept involves conversion of the solid biomass to a clean fuel gas, using a biomass gasifier. The gas can be combusted in the same furnace as the coal. For this reason, it is also possible to use biomass, which, for example, is difficult to grind. The gas can be cleaned and filtered before use, to remove any impurities.

The parallel co-firing concept involves the installation of a completely separate biomass boiler for increasing the steam parameters, like pressure or temperature, in the steam system of the coal power plant. This method allows the use of a high amount of biomass.

Biomass co-firing is a good method to minimize greenhouse gases, because this process reduces emissions of net carbon dioxide, methane, sulfur oxide, and nitrogen oxide. In addition, existing coal power plants can be retrofitted with minimal (if any) reduction of boiler efficiency after adjustment to the new fuel mixture. However, biomass co-firing also faces some challenges such as (i) fuel supply, fuel handling, and fuel storage as well as (ii) a potential increase in corrosion and (iii) ash deposition.

See also: Combustion.

Cogeneration

Cogeneration is the simultaneous production of heat and electricity, commonly called combined heat and power (CHP), from a single fuel. Cogeneration is a very efficient technology to generate electricity and heat simultaneously.

Using a fuel to simultaneously generate heat and electricity with a single unit is more efficient and cost-effective than generating heat and electricity separately in two different units.

More specifically, cogeneration usually entails the use of what would otherwise be waste heat (such as an exhaust from a manufacturing plant) to produce additional energy benefit, such as to provide heat or electricity for the building in which it is operating. Cogeneration is also for the environment insofar as recycling the waste heat saves other potential pollutant-generating fuels from being burned.

Traditionally, a steam turbine is used to produce electricity, although a wood gasification/internal combustion unit can also be a cogeneration unit. Several factors affect the economic feasibility of a combined heat and power unit including wood waste disposal problems, high electricity costs, and year-round steam use. More electricity and heat are generated for a lesser amount of fuel by a combined heat and power unit than by a separate heat and power (SHP) unit.

The common challenges for all wood-fired systems are ensuring adequate fuel procurement and solving the complex fuel handling and storage issues.

See also: Combustion.

Cohesive Energy Density

The cohesive energy density is the amount of energy that is needed to completely remove the unit volume of molecules from their neighbors to infinite separation (an ideal gas). This is equal to the heat of vaporization of the compound divided by its molar volume in the condensed phase.

Thus, the cohesive energy density (c) of a liquid fuel is a numerical value that indicates the energy of vaporization in calories per cubic centimeter, and is a direct reflection of the degree of van der Waals forces holding the molecules of the liquid together and can be derived by the following expression:

$$c = (\Delta h - RT)/v_m$$

In this equation, c is the cohesive energy density, Δh is the heat of vaporization, r is the gas constant, t is the temperature, and v_m is the molar volume.

The correlation between vaporization and van der Waals forces also translates into a correlation between vaporization and solubility behavior because the same intermolecular attractive forces have to be overcome to vaporize a liquid as to dissolve it. Since the solubility of two materials is only possible when their intermolecular attractive forces are similar, one might also expect that materials with similar cohesive energy density values would be miscible.

Cold Pelletizing

A cold pelletizing process for the carbonization of solid fuel pellets involves heating the pellets to 550 to 650°C (1,020 to 1,200°F) and subsequently carbonized with sand as a heat carrier. Another process involves the conversion of process (solid) fines into pellets. In the second stage, the pellets are coated with hematite ore (Fe_2O_3) and the ore-covered pellets are then coked whereupon they are softened and sintered together to form a coherent coke. The addition of a viscous oil to the mix increases the stability of the pellets in the oven. The amount of ferric oxide (Fe_2O_3) is critical, and a definite level exists that cannot be exceeded if the pellet is to retain the shape.

Combustion

All fuels contain two combustible constituents: the volatile matter and char. As the temperature of the fuel rises, the volatile matter is released in the form of vapors or vaporized tars and oils. The spurts of flame, for example, as wood burns, are an indication of the combustion of these products.

After this process ends, the solid remnants comprise of char and inert matter. The char, which is mainly carbon, can be further combusted to produce heat and carbon dioxide. The inert matter then becomes clinker, slag, or ashes.

Fuel preparation → combustion → boiler → engine or turbine

Mass burn combustion (MBC) can use municipal solid waste (MSW) to generate electricity. This is one of the main methods of incineration and has been around for years. It is commercially available and has been optimized. The plant operates by feeding waste onto a moving grate where it is burned; the heat generated by this is used to generate steam that drives a generator to produce electricity. Burning the waste produces two types of ash: (i) bottom ash and (ii) fly ash.

Incinerator bottom ash falls through the grate for collection and is either landfilled or used in the construction industry. Fly ash, which escapes with the flue gases that are emitted to the atmosphere, can contain sufficient dioxins and metals that require cleaning. As it involves the mass burning of MSW, this has many concerns attached to it. In particular, the waste is a mixture of different materials; if these are combusted, they may have a detrimental effect on the environment. The main pollutants that result from municipal solid waste are (i) gases, (ii) metals, (iii) organic compounds, and (iv) particulate matter.

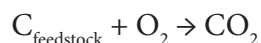
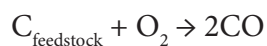
An area of environmental concern is the contents of the array of gases that are emitted from the plants. The gases contain dioxins, which are suspected of causing many health problems including cancer. Another environmental issue is the particulate matter, focusing particularly on ultra-fine particles less than ten millionths of a meter in diameter. These are often inorganic materials with metals and organic compounds on their surface.

See also: Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Fouling – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

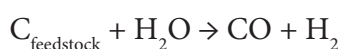
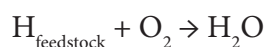
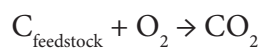
Combustion - Chemistry

Combustion occurs, chemically, by initiation and propagation of a self-supporting exothermic reaction. The physical processes involved in combustion are principally those which involve the transport of matter and the transport of energy. The conduction of heat, the diffusion of chemical species, and the bulk flow of the gas all follow from the release of chemical energy in an exothermic reaction. Thus, combustion phenomena arise from the interaction of chemical and physical processes.

The first requirement, somewhat difficult with some feedstocks because of the molecular complexity, is that the overall stoichiometry of the reaction must always be established. For these purposes, the feedstock is usually represented by carbon which can react with oxygen in two ways, producing either carbon monoxide or carbon dioxide.

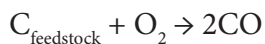


In direct combustion, the feedstock is burned (i.e., the carbon and hydrogen in the feedstock are oxidized into carbon dioxide and water) to convert the chemical energy of the feedstock into thermal energy after which the sensible heat in the products of combustion can then be converted into steam that can be external work or directly into shaft horsepower (e.g., in a gas turbine).

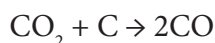


In fact, the combustion process actually represents a means of achieving the complete oxidation of the feedstock.

On a more formal basis, the combustion process may be simply represented as the staged oxidation of feedstock carbon to carbon dioxide with any reactions of the hydrogen in the feedstock being considered to be of secondary importance.



The stoichiometric reaction equations are quite simple, but there is a confusing variation of hypotheses related to the sequential reaction mechanism which is caused to be a great extent by the heterogeneous nature (solid and gaseous phases) of the reaction. But, for the purposes of this text, the chemistry will remain simple as shown in the above equations. Other types of combustion systems may be rate-controlled due to the onset of the Boudouard reaction.

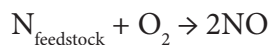
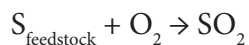


In more general terms, the combustion of carbonaceous materials (which contain hydrogen and oxygen as well as carbon) involves a wide variety of reactions between the many reactants, intermediates, and products. The reactions occur simultaneously and consecutively (in both forward and reverse directions) and may at times approach a condition of equilibrium. Furthermore, there is a change in the physical and chemical structure of the fuel particle as it burns. Also, the characteristics and physical properties of the combustion products vary. In general, the size, shape, and chemical composition of these materials determine their beneficial reuse as a component of building materials or as a replacement to other virgin materials such as sand, gravel, or gypsum.

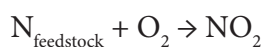
The beneficial use of the combustion products involves the use of or substitution of the combustion products for another product based on performance criteria. Using combustion products can generate significant environmental, economic benefits. Beneficial use includes raw feed for cement clinker, concrete, grout, flowable fill, structural fill, road base/sub-base, soil-modification, mineral filler, snow and ice traction control, blasting grit and abrasives, roofing granules, mining applications, wallboard, waste stabilization/solidification, soil amendment, and agriculture.

The complex nature of biomass as a molecular entity has resulted in the chemical explanations of the combustion process being confined to the carbon in the system and, to a much lesser extent with only passing acknowledgment of the hydrogen and other elements, but it must be recognized that the system is extremely complex and that the heteroatoms (nitrogen, oxygen, and sulfur) can exert an influence on the combustion and it is this influence that can cause serious environmental concerns.

For example, the conversion of the feedstock-bound sulfur and nitrogen (in addition to any reactions or aerial nitrogen with aerial oxygen under the prevailing conditions) to their respective oxides during combustion is a major environmental issue.



Thus:



The release of the sulfur and nitrogen from the feedstock is not as simple as represented here, and the equations are simplifications of what are, presumably, complex processes.

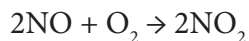
The sulfur dioxide that escapes into the atmosphere is either deposited locally or is converted to sulfurous and sulfuric acids by reaction with moisture in the atmosphere.



Thus:



Nitrogen oxides also contribute to the formation and occurrence of acid rain, in a manner similar to the production of acids from the sulfur oxides, yielding nitrous and nitric acids.



Thus:



In addition to causing objectionable stack emissions, the ash produced during the process and volatile inorganic material generated by thermal alteration of mineral matter in coal will adversely affect heat transfer processes by fouling the heat-absorbing and radiating surfaces and will also influence the performance of the combustion system by causing corrosion, and operating procedures must therefore provide for effective countering of all these hazards.

See also: Combustion, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Fouling, Combustion – Fouling – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Direct

Direct combustion is a thermochemical technique in which (in the current context) biomass is burned in open air or in the presence of excess air. In this process, the photosynthetically stored chemical energy of the biomass will be converted into gases. Generally, direct combustion is carried out inside a furnace, steam turbine, or boiler at a temperature range of 800 to 1,000°C (1,470 to 1,830°F). This process is suitable for all types of biomass, which has low moisture content (<50%).

Electricity production by direct combustion is the simplest process when dry biomass is burned in co-combustion with coal. This transformation path has the lowest impacts on the environment, but it is important to notice that in this study, the needed heat to dry the biomass comes from the recovery of flue gas. Hence, it is not accounted for in the environmental balance or the energetic balance and, in addition, this approach is likely to produce high quantities of nitrogen oxides.

Another possibility for sustainable operation of microalgae biomass in direct combustion is coal–algae cofiring which has the potential to reduce the emission of carbon dioxide by recycling the carbon dioxide from

the combustion process to microalgae cultivation. This leads to lower emission of greenhouse gases into the atmosphere.

See also: Direct Combustion.

Combustion – Effect of Additives and Catalysts

Additives may catalyze or otherwise affect combustion processes. For example, salt has long been known to be of some assistance in removing soot deposits from surfaces and the catalysis of the process in which alkali salts serve to catalyze the carbon-steam reaction to produce synthesis gas (carbon monoxide/hydrogen mixtures). This mixture may then, in turn, react to produce hydrocarbon derivatives and oxygenated materials in the presence of the multitude of trace metals that can (and do) occur in biomass and waste.

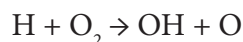
In addition to causing objectionable stack emissions, the ash and volatile inorganic material generated by thermal alteration of mineral matter in the feedstock will adversely affect heat transfer processes by fouling heat-absorbing and radiating surfaces and will also influence the performance of the combustion system by causing corrosion, and operating procedures must therefore provide for effective countering of all these hazards.

Corrosion is mainly caused by oxides of sulfur, but in certain parts of a combustion system, specifically on furnace wall tubes with metal temperature of 290 to 425°C (550 to 800°F) and superheater or reheater tubes with temperatures in the range 600 to 700°C (1,110 to 1,300°F), corrosion can be induced by tube deposits that destroy protective surface oxide coatings.

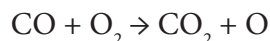
Corrosion damage that is usually ascribed to sulfur is actually caused by sulfuric acid, which is generated from organic and inorganic sulfur-bearing compounds:



Oxidation of sulfur dioxide to sulfur trioxide occurs mostly in flames where (transient) atomic oxygen species are thought to be prevalent by interactions of hydrogen atoms with oxygen:



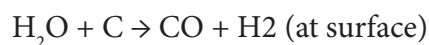
as well as by interactions of carbon monoxide with oxygen:



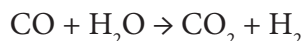
The process can be catalyzed by the ferric oxides which form on boiler tube surfaces and show excellent catalytic activity for sulfur dioxide oxidation at approximately 600°C (1110°F), i.e., at temperatures which occur in the superheater section of a boiler.

The presence of water has a marked effect on combustion (by participating in various combustion reactions), and there is evidence for the existence of active centers for chain reactions involved in the further combustion of carbon monoxide and hydrogen (which would be reaction intermediates in the combustion process). It is generally assumed that moisture catalyzes the oxidation of coal.

The endothermic steam-carbon reaction is primarily responsible for cooling effects in furnaces, and the presence of moisture is believed to cause heat generation at the surface of the bed and in the combustion by virtue of the (endothermic) formation of carbon monoxide and hydrogen in the bed which then burn at the surface. On the other hand, the presence of water vapor appears to assist in the formation of carbon dioxide:

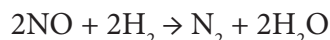
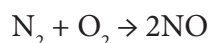
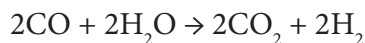


Moisture appears to play a more integral role in the combustion of hydrogen-deficient carbonaceous fuels than has been generally recognized. The carbon-steam reaction to produce carbon monoxide and hydrogen (which are then oxidized to the final products) is an important stage in the combustion sequence as is the carbon monoxide shift reaction to yield carbon dioxide and hydrogen:



Since the whole system involves reaction (and equilibria) between the fuel (i.e., carbon), water, carbon monoxide, hydrogen, and carbon dioxide, the rapid rates of the reactions render it difficult (if not impossible) to determine precisely which of the reactions are the major rate-controlling reactions. In addition, the heterogeneous nature of the system adds a further complication.

The presence of inert gases would usually be expected to dilute the reactants and therefore diminish the reaction rates; such inert materials may actually, on occasion, accelerate the reaction(s). Indeed, the addition of nitrogen to the reaction mixture can be as effective as the addition of oxygen. The nitric oxide formed in the mixture is believed to act as a catalyst:



See also: Combustion, Combustion – Chemistry, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Fouling – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Environmental Aspects

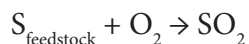
The environmental aspects of combustion have been a major factor in the various processes. Large amounts of feedstocks are consumed in generating electricity, and the emissions from power stations and similar industrial sources represent a potential, and considerable, environmental hazard. These power plants emit effluents, which often are pollutants and which by mere contact with the external environment or by (generally) simple atmospheric chemical transformations, may form secondary pollutants that are more harmful than the initial effluent/pollutant.

The gaseous emissions resulting from the complete combustion of a carbonaceous feedstock are carbon dioxide and water. However, in the exhaust gases from any practical device, there will be, in addition to these compounds, carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), unburned hydrocarbon derivatives, and probably particulate matter (soot). The *lifetime* of these species in the atmosphere is relatively short, and if they were distributed evenly, their harmful effects would be minimal.

Unfortunately, these man-made effluents are usually concentrated in localized areas and their dispersion is limited by both meteorological and topographical factors. Furthermore, synergistic effects mean that the pollutants interact with each other: in the presence of sunlight, carbon monoxide, nitrogen oxide(s), and unburned hydrocarbon derivatives lead to photochemical smog, while when sulfur dioxide concentrations become appreciable, sulfur oxide-based smog is formed. It is worth remembering that the non-toxic, but non-life supporting and suffocating, carbon dioxide may have an important effect on the environment. The surface of the earth emits infrared radiation with a peak of energy distribution in the region where carbon dioxide is a strong absorber. This results in the situation whereby the atmosphere traps this infrared radiation, and the temperature of the surface of the Earth is increased.

The three major types of pollutants emitted by the combustion process are particulate matter, sulfur dioxide, and nitrogen oxides (NO_x). Particulate matter arises from minerals in the feedstock that are converted in the combustion process to finely divided fly ash which can be carried out of the stack with the hot exhaust gases; the practice of burning finely divided feedstock contributes to fly ash emissions. There is also the concept that the size of the fly ash has a direct bearing on the physical and chemical properties that can influence the method of disposal.

Sulfur dioxide is produced by the oxidation of organic sulfur in the feedstock and is normally cited as the most troublesome of the pollutants. For example, sulfur dioxide produced in the combustion process reacts with water to produce sulfurous acid and with oxygen and water in the atmosphere to yield sulfuric acid:



sulfurous acid

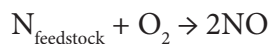


sulfuric acid

Sulfuric acid contributes to the harmful and extrusive acid rain, often many hundreds of miles from the original source. Sulfur dioxide levels in the flue gas from large furnaces and boilers may be as high as 2,000 ppm. At flame temperatures in the presence of excess air, some sulfur trioxide is also formed:



Only a small amount of sulfur trioxide can have an adverse effect as it leads to the condensation of sulfuric acid and causes severe corrosion. Although diminution of the excess air reduces sulfur trioxide formation considerably, other considerations, such as soot formation, dictate that the excess air level cannot be lowered sufficiently to eliminate sulfur trioxide entirely. For the most part, the nitrogen that is inherent in the organic structure of the feedstock is converted to nitrogen oxides during combustion which also produce acidic products, thereby contributing to the acid rain phenomenon:



nitrous acid



nitric acid

Fluidized-bed combustion generates little, if any, thermal de-NO_x despite the long residence times since the bed temperatures are usually too low; any residual nitrogen oxide is often derived from the fuel nitrogen rather than from the aerial nitrogen.

Although not generally considered to be a major pollutant, hydrogen chloride from inorganic contaminants is gaining increasing recognition as a pollutant arising from the combustion process. Hydrogen chloride quickly picks up water from the atmosphere to form droplets of hydrochloric acid and, like sulfur dioxide, is a contributor to acid rain. However, hydrogen chloride may exert severe local effects because it does not have to undergo any chemical change to become an acid.

Under atmospheric conditions involving a buildup of stack emissions in the area of a large power plant, the concentration of hydrochloric acid in rain droplets could be quite high. Little, if anything, can be done as part of the feedstock pretreatment operation(s) to eliminate nitrogen because this element is a part of the organic structure of the feedstock. The situation is less clear in the case of hydrogen chloride sources in the feedstock. Both organically-bound chlorine and inorganic chloride salts contribute appreciably to hydrogen chloride formation during combustion, but these processes do not remove organically-bound chlorine, which is a more likely precursor to hydrogen chloride in a combustion process.

Appropriate processing can reduce both the mineral matter (the precursor to the ash) and the sulfur content. As with inorganic chlorides, washing processes are the most successful methods for removing inorganic sulfur but they do not affect the organic sulfur content. Most stack gas scrubbing processes are designed for sulfur dioxide removal; nitrogen oxides are controlled as far as possible by modification of combustion design and flame temperature regulation. However, processes for the removal of sulfur dioxide usually do remove some nitrogen oxides; particulate matter can be removed efficiently by commercially well-established electrostatic precipitators.

There are several processes for the removal of sulfur dioxide from stack gas, but scrubbing process utilizing limestone (CaCO_3) or lime [$\text{Ca}(\text{OH})_2$] slurries has received more attention than other stack gas scrubbing processes. Attempts have been made to use dry limestone or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) within the combustor as an “in situ” method for sulfur dioxide removal, thus eliminating the wet sludge from wet processes. This involves injection of dry carbonate mineral with the feedstock followed by recovery of the calcined product along with sulfite and sulfate salts:



The various solid products are removed by standard means, including cyclone separators and electrostatic precipitators.

The non-volatile oxidation products of the inorganic constituents of the feedstock (such as sodium and potassium) are left as oxides in the combustion ash and contribute to the formation of corrosive deposits. When the feedstock is pulverized prior to the combustion process, a large proportion of the ash is carried out of the combustion chamber with the exhaust gas stream and has to be removed as completely as possible, usually by use of electrostatic precipitators. The removal of fly ash from combustion effluent streams is as important to the environment as the removal of sulfur oxides and nitrogen oxides. If not removed, the inorganic constituents and the organic constituents of the ash can cause serious environmental consequences, in addition to the solid particles acting as condensation nuclei and (catalytic) surfaces for the conversion of sulfur dioxide to the trioxide:



Because of its organic origin of the feedstock and its intimate co-mixture with mineral, the biomass feedstock may contain a large number of elements in minor or trace quantities. In regard to the behavior of trace elements in biomass, the elements have been divided into two groups, those appearing mainly in the bottom ash (elements or oxides having lower volatility) and those appearing mainly in the fly ash (elements or oxides having higher volatility).

For power plants using dry particulate collection devices, such as electrostatic precipitators, it was believed that the most volatile elements (such as mercury and selenium) could actually escape in the elemental state with the flue gas; wet scrubbers, however, were believed capable of removing most of the elements from the gas streams and transferring them to the liquid effluent. Essentially no particulate matters from the combustion process should be ejected into the atmosphere; all particulate streams should be collected and either returned to the combustors, where they melt and are removed as slag, or are removed as fly ash.

Any eventual dispersion of the elements present depends on the possibility of leaching. The concern, therefore, is to identify elements that may be occurring in the gaseous state. Among the trace elements that may be present in combustion feedstocks (such as biomass and waste) with recognized toxic properties, high-volatility elements (beryllium, mercury, and lead) do not form gaseous-hydrides, will condense on cooling, and likely will be almost completely removed by the aqueous condensates formed on gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous hydrides, (covalent) hydrides: arsine, Stibine, and hydrogen selenide. These however, have stability characteristics that preclude their formation at the temperature and pressure prevailing in the oil/gas plant gasifiers.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Fluidized Bed, Combustion – Fouling, Combustion – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Fluidized Bed

Fluidized bed combustion (fluid bed combustion, FBC) is a combustion technology in which a fluidized bed suspends the solid fuel on upward-blowing jets of air during the combustion process. The result is a turbulent mixing of gas and solids.

The tumbling action, much like a bubbling fluid, provides more effective chemical reactions and heat transfer. Fluid bed combustors are more flexible than conventional plants in that they can be fired on biomass as well as coal. Fluid bed combustion systems fit into two major groups which are (i) atmospheric systems – the fluidized bed combustor and (ii) pressurized systems – the pressurized fluidized bed combustor.

Atmospheric fluidized bed systems use limestone or dolomite to capture sulfur released during the combustion. Jets of air suspend the mixture of sorbent and burning coal during combustion, converting the mixture into a suspension of red-hot particles that flow like a fluid.

Pressurized fluid bed systems also use a sorbent and jets of air to suspend the mixture of sorbent and burning coal during combustion. However, these systems operate at elevated pressures and produce a high-pressure gas stream at temperatures that can drive a gas turbine. Steam generated from the heat in the fluidized bed is sent to a steam turbine, creating a highly efficient combined cycle system.

Fluid bed combustion reduces the amount of sulfur emitted in the form of sulfur dioxide emissions. Limestone can be used to precipitate out sulfate during combustion, which also allows more efficient heat transfer from the boiler to the apparatus used to capture the heat energy (usually water tubes). The heated precipitate coming in direct contact with the tubes (heating by conduction) increases the efficiency. Since this allows the process to use lower temperatures (approximately 800°C/1,500°F), less nitrogen oxide is also emitted. However, burning at low temperatures also causes increased polycyclic aromatic hydrocarbon emissions.

This method of incineration uses is a viable alternative to the mass burn system. The pellets are fed onto a bed consisting of a mixture of sand and dolomite mineral. Air is then pumped through the whole mixture to create a bubbling liquid. The waste in this new liquid form has an improved combustion efficiency that reduces pollution and increases generation per ton of waste. This type of system may be slower than moving bed combustion.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fouling, Combustion – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Fouling

Fouling is the accumulation of small, sticky molten particles of coal ash on a boiler surface.

Coal combustion is, on the one hand, a balance of high reaction or flame temperatures which favor carbon monoxide at equilibrium and, on the other hand, the use of excess air which drives the conversion to carbon dioxide. Relative to these two opposing reactions, the rates of reaction are generally controlling and manifested by short residence times with rapid heat transfer such that the system temperature is lowered before equilibrium can occur,

hence the consideration that (complete) combustion is a non-equilibrium process. This is contrary to gasification by partial combustion, which occurs at lower temperatures and longer residence times without heat transfer (the system remains adiabatic), where equilibrium conditions tend to apply.

Though thermodynamic and rate calculations may be used to maximize flame temperatures and conversions, it is the empirical observation and evidence in each situation that will dictate the optimum air-to-fuel ratio and will depend on fuel analysis including moisture, air humidity and temperature, and other general operating variables. Although 15 to 25% v/v excess air is a median range, it depends not only on the fuel but also on the type of combustion system and the control of that system.

The ash is composed mostly of metal oxides, and the composition affects the softening point. Iron oxides are a particular source of problems, and the reducing atmosphere ($\text{CO} + \text{H}_2$; produced by the water gas reaction) in the fuel bed serves to reduce ferric oxide (Fe_2O_3) to ferrous oxide (FeO) with the production of *clinker* which will contribute to reactor fouling.

In addition, the fouling of combustion systems has also been related to the alkali metals content of biomass and waste. For example, a feedstock with a total alkali metal content on the order of <0.5% w/w (as equivalent sodium oxide, Na_2O) produces deposits that can be removed by the action of soot blowers (perforated lances through which jets of high-pressure air or steam can be sent between boiler tubes), but for a feedstock having more than 0.6% w/w alkali metal (as equivalent sodium oxide), the deposits can increase markedly and can be a major problem.

To combat fouling, modern combustion equipment is designed to ensure that particles are cooled to well below their fusion temperatures before they can reach the banks of closely spaced tubes in the upper regions of the boiler. In pulverized fuel systems, provision is usually made for tilting the burners and thereby periodically altering the heat regime. In addition, tube deposits are routinely dislodged by frequent *soot blowing*.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Heat Balance

The heat balance of the combustion process provides a relative weighting of the heat input into the system versus the heat output of the process:

$$dH_I \rightarrow dH_c + S_H + dH_E$$

In this equation, dH_c is the heat input, S_H is a composite of the sensible and latent heats of air, fuel, and other materials, and dH_E is the heat from exothermic reactions (other than combustion) which may contribute to the overall combustion process:

$$dH_o \rightarrow dH_{cu} + S_{HC} + dH_{-E} + dS_{AG} + dH_L$$

Here, dH_o is the heat output, dH_{cu} is the heat of combustion of unburned fuel, S_{HC} is the sensible and latent heats in the carbonization products, dH_{-E} is the heat absorbed by endothermic reactions, dS_{AG} is the sensible and latent heats in the combustion products (ash and stack gases), and dH_L is the heat losses to the surroundings by convection, radiation, and combustion.

The presence of water vapor in the combustion system appears in the latent heat effects, and one consequence of high moisture content in coal combustion is that a part of the heat is lost due to evaporation of the moisture in the coal and is not recouped from the combustion products. A small amount (<5% w/w) of water in the feedstock may not exert any marked effect on the overall heat requirements, since the sensible heat of the gases vaporizes the water.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Ignition

The ignition of the carbonaceous feedstock has been described as occurring in just a few hundredths of a second with the onset of burning in less than half a second. The ignition distance has been observed to be on the order of 0.04 in (1 mm) with the carbon monoxide formed by reaction at the surface burning to carbon dioxide at distances close to the surface (0.5 to 4 mm). Water is evaporated in the initial stages, and the ignition is propagated through a dry bed.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Heat Balance, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Influence of Feedstock Quality

Feedstock quality is recognized as having an impact, often significant, on combustion, especially on many areas of the combustion system. The parameters of carbon content, hydrogen content, rank, mineral matter content (ash content), sulfur content, and moisture content are regarded as determining factors in combustibility as it relates to both heating value and ease of reaction.

Finally, since feedstock quality can be affected by oxidation or weathering, the question is raised related to the effects of oxidation and weathering on combustion and whether oxidized feedstock could maintain a self-sustaining flame in an industrial boiler. The inhibition of volatile matter release due to changes in the char morphology as a result of the oxidation/weathering suggests that this may not be the case.

One option for managing feedstock quality is to blend one particular feedstock with others until a satisfactory quality is achieved. This is similar to current crude oil refinery practice where one refinery actually accepts a blend of various crude oils and operates on the basis of average feedstock composition.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Heat Balance, Combustion – Ignition, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Mechanism

The exact nature of the combustion process is difficult to resolve but can be generally formulated as two processes which are (i) the degradation of hydrogen, and (ii) the degradation of carbon. It is also necessary to understand the surface chemistry involved in the burning process, and progress is being made in this direction. However, biomass and waste feedstocks being heterogeneous solids add an increasingly difficult dimension to the combustion chemistry and physics; combustion actually occurs on the surface with the oxidant being adsorbed there prior to reaction. However, the initial reaction at (on) the surface is not necessarily the rate-determining step; the process involves a sequence of reactions, any one of which may control the rate.

The initial step is the transfer of reactant (i.e., oxygen) through the layer of gas adjacent to the surface of the particle. The reactant is then adsorbed and reacts with the solid after which the gaseous products diffuse away from the surface. If the solid is porous, much of the available surface can only be reached by passage of the oxidant along the relatively narrow pores and this may be a rate-controlling step. Rate control may also be exercised by: (a) adsorption and chemical reaction, which are considered as chemical reaction control; and (b) pore diffusion, by which the products diffuse away from the surface. This latter phenomenon is seldom a rate-controlling step.

In general, rate control will occur if the surface reaction is slow compared with the diffusion processes; while diffusion shows a less-marked temperature dependence, reaction control predominates at low temperatures, but diffusion control is usually more important at higher temperatures. In fact, on a chemical basis, hydrogen degradation outweighs the slower-starting carbon degradation in the early, or initial, stage of combustion. But, at the same time, the carbon monoxide/carbon dioxide ratio is decreased.

After the initial stages of combustion, during which volatile material is evolved (which is also combustible), a nonvolatile carbonaceous residue (coke, char), which can comprise up to 90% of the original mass of the feedstock, remains. During the combustion of the coke, three different zones (regimes) of combustion can be distinguished.

In the first zone (I), the rate of diffusion to and away from the surface is fast compared with the rate of the surface reaction; such phenomena are observed at low temperatures. At much higher temperatures, the rate at which oxygen molecules are transported from the bulk gas to the external surface is slow enough to be rate controlling (Zone III); the observed rate can be equated to the molar flux of oxygen to unit area of external surface. Finally (Zone II; intermediate between I and III), the oxygen transport to the external surface is rapid but diffusion into the pores before reaction is relatively slow.

In practice, there are considerable differences between the reactivity of different cokes, some of which can be assigned to variations in pore structure and others to the presence of impurities (e.g., alkali metal salts) which have a pronounced catalytic effect on the surface reaction. Consequently, the temperature ranges corresponding to the three zones differ and are not constant for different cokes/chars.

There are alternate ways to consider the mechanism of combustion, and there is a variety of models proposed for this purpose. For example, in a simple model for the combustion process, the initial step is assumed to be (i) devolatilization, (ii) ignition, and (iii) rapid burning of the volatiles relative to the char. But the actual mechanism is considered to be somewhat more complex. The process is thought to consist of (i) diffusion of reactive gases to the carbon surface, (ii) adsorption, (iii) formation of transitory complexes, and (iv) desorption of the products, but the overall reaction mechanism for a devolatilized char particle is believed to be (i) transport of oxygen to the surface of the particle, (ii) reaction with the surface, and (iii) transport of the products away from the surface.

As the pressure of the system is increased, the mechanism tends toward diffusion control. This is due to the mass transfer or diffusion rate coefficient being inversely proportional to pressure. The overall rate, however, will increase due to the increased oxygen partial pressure at the higher pressures.

The complexity of many carbonaceous feedstocks has resulted in treatments of the combustion process being confined to the carbon in the system and, to a lesser extent, the hydrogen, but it must be recognized that the system is extremely complex. Even with this simplification, there are several principal reactions that are considered to be an integral part of the overall combustion process.

In summary, it is more appropriate to consider the combustion of carbonaceous materials (which contain carbon, hydrogen, nitrogen, oxygen, sulfur, and mineral matter) as involving a variety of reactions between (i) the reactants, (ii) the intermediate, or transient, species, and (iii) the products. The reactions can occur both simultaneously and consecutively (in both forward and reverse directions) and may even approach steady-state (equilibrium) conditions. Moreover, there is a change in the physical and chemical structure of the fuel particle during the process.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Soot Formation, Combustion – Surface Effects.

Combustion – Soot Formation

The formation and possible emission of soot is often observed during combustion of fuels, such as biomass and waste. Soot consists of carbonaceous particles formed during combustion, and can be identified in flames and fires as yellow luminescence. In modern practical combustion devices, the formation of soot is mostly an unwanted process, since strict legislation on emission levels applies, and soot is known to play a significant effect on health.

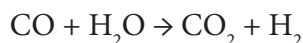
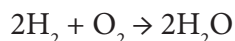
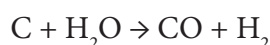
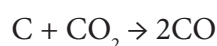
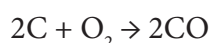
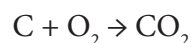
Soot formation involves several steps which are (i) the construction of a sub-nanometer polycyclic aromatic hydrocarbon derivatives, sometimes referred to as seeds, (ii) the growth of that small seed to the size of a few nanometers as it passes through a mixture of unburned or partially burned molecules, and (iii) the self-agglomeration of these larger particles to form particles tens to hundreds of nanometers in size. The first step of seed construction that is thought to proceed through at least two mechanisms and which mechanism dominates under different conditions that are not accurately known.

Combustion – Surface Effects

The ignition of a carbonaceous feedstock has been described as occurring in just a few hundredths of a second with the onset of burning in less than half a second. The ignition distance has been observed to be on the order of 0.04 in (1 mm) with the carbon monoxide formed by reaction at the surface burning to carbon dioxide at distances close to the surface (0.5–4 mm). Water is evaporated in the initial stages, and the ignition is propagated through a dry bed.

The conditions under which a feedstock ignites and the behavior during ignition will relate to (i) the structure of the volatilized constituents and (ii) the temperature in the coke-burning state. In addition, some consideration must be given to the manner in which the volatile matter is released. For example, the particle may burn by first releasing all the volatile matter which may burn simultaneously with the carbon. It does, however, seem unlikely that oxygen would reach the surface in the presence of volatiles and, thus, any oxygen attempting to diffuse through the volatiles layer would react instead.

Generally, it is possible to subdivide the overall reaction sequence into (i) those reactions which could conceivably occur at the surface of the char and (ii) those reactions which may occur between the gaseous products themselves.



During combustion, there are several possibilities for the mode in which the carbon reacts in the particle structure. The carbon may react only from the surface, and reaction may proceed uniformly throughout the particle, or, alternately, the particle may be regarded as a hollow sphere with burning occurring on both the outer and inner surfaces. In fact, there is evidence that particles do form hollow spheres during combustion and such spheres (cenospheres) are believed to be formed during volatilization. The porous structure of the carbonized char also exerts an effect on the burning operation as does particle temperature up to several hundred degrees above the gas temperature.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation.

Combustion Technologies

Stokers currently used in wood-fired applications fall into two major categories, the air-cooled traveling grate and water-cooled stationary grate. With both of these types of stokers, the wood fuel is distributed across the width of the grate with metering bins on the front wall of the boiler. The fuel is then uniformly distributed over the depth of the grate by air-swept spouts.

Sawdust and other fines in the fuel are burned in suspension, while larger particles drop to the grate and are dried and burned directly on the grate surface. Heated low-pressure combustion air is evenly distributed through the grate surface to promote fuel drying and provide the primary source of combustion air. To further aid the combustion

process, high-pressure over fire air ports are used above the grate to provide turbulence and thorough mixing of the unburned combustion gases with air.

With the traveling stoker, the grate travels from the rear of the boiler to the front with fuel being fed across the depth of the furnace to the rear wall. Ash travels to the front edge of the grate and falls into a pit. This design requires additional maintenance due to the high temperatures that the grate bars are exposed to and the abrasive nature of the wood ash due to the high silica content.

The Detroit hydro-grate stoker typifies the stationary water-cooled grate. With this design, the grate bars are attached to a water-cooled tubular grid and the grate is sloped at a slight angle (approximately 6-8 degrees) and is periodically vibrated to assist the movement of the burning fuel and ash down the grate toward the ash pit. The advantage of a water-cooled grate is the reduced maintenance from the minimum of moving parts. Care must be taken in operation not to permit an ash pit fire. This will result in overheating and failure of the water supply tubes feeding the grate's support grid.

Both of these two types of stokers are commercially proven technologies that are highly flexible in the choices of fuels that can be burned, alone or in combination. Turndown and response to rapid load swings with little or no change in steam temperature or pressure are also good.

The application of wood-fired circulating fluidized bed boilers (CFB) has generally been limited to waste wood products that are significantly drier than biomass from the forest. Typically, circulating fluidized bed boilers use fuels such as demolition wood waste and mill residues but they can be easily designed to fire higher moisture wood fuels, alone or in combination with other solid fuels.

In a circulating fluidized bed boiler unit, fuel is fed into the lower part of the furnace. The fuel mixes with the fluidized bed where the solids are maintained at 815 to 870°C (1,500 to 1,600°F). The fuel introduced to the bed is quickly heated until it reaches ignition temperature. As the fuel burns, the size is reduced to a point where the particles are entrained by the upward flow of combustion gases. Larger particles are removed from the gas stream before it reaches the convection surfaces of the unit by use of a cyclone or particle collector beams, and they are returned to the bed for further burnout and size reduction. The advantages of a circulating fluid bed unit includes the ability to burn lower grade fuels at reduced temperatures and excess air without loss of combustion efficiency. In addition to the reduced NO_x and SO_x emissions that are inherent with a circulating fluid bed, these units can burn high-fouling fuels without the normally associated operating problems due to the reduced combustion temperatures. Circulating fluid bed units will suffer from bed sintering from firing fuels that have high alkali metal content. This will result in higher fouling of the bed tube surfaces and excessive above bed burning that will increase furnace exit gas temperatures and superheater fouling. Units equipped with refractory lined cyclones will also have high refractory maintenance requirements due to the abrasive nature of the ash.

The application of wood-fired bubbling fluidized bed boiler (BFB) units is much more widespread than the circulating fluid bed units. Due to their ability to burn high moisture, low-Btu fuels, they have been uniquely suited to the needs of the pulp and paper industry to burn biomass, wood waste, and bark commonly produced in large quantities at a pulp mill.

The fuel feeding and combustion process for a bubbling fluid bed unit is similar to that of a circulating fluid bed unit except that the bed is only partially fluidized, and the burning fuel is not entrained in the combustion gas flow and remains in the bed. The advantage of a bubbling fluidized bed unit is its ability to burn difficult low-grade wet fuels. The thermal inertia of the bed and the mechanical action of the sand and ash to break down the fuel particles make a bubbling fluidized bed unit insensitive to fuel variations. Unlike a circulating fluid bed unit, a bubbling fluid bed unit utilizes a non-circulating bed in the furnace bottom that is made up of sand. The wood ash and a small amount of sand are removed through a drain opening in the floor of the furnace to control the bed level. The sand acts as a thermal reservoir, and it mechanically breaks down the size of the fuel to facilitate combustion. Bubbling fluid bed units do suffer from the same bed sintering problems as the circulating fluid bed units, but due to the partially fluidized bed, the sintering problems can be much worse and can result in high sand consumption rates due to the high bed drain rates.

The inclined fluidized bed (IFB) technology combines aspects of the inclined grate and fluidized bed technologies. Unlike most other technologies that mechanically agitate the fuel during combustion, the inclined fluidized bed uses an entirely different concept for performing this function. With the inclined fluidized bed technology, the fuel

is fed onto an inclined grate assembly via a feed ram where controlled combustion takes place. Combustion air is provided to each portion of the grate from a combustion air fan through slots in the grate assembly.

The inclined fluidized bed grate utilizes hollow tubes to form the steps on the grate. Each of the tubes is equipped with a number of small nozzles that provide a passage from the tubes to the fuel bed on the grate. The tubes are connected to a common fan that recycles a portion of the exhaust gas. This gas is introduced into the fuel bed as short pressure pulses, controlled by valves on an intermittent basis, providing a burst of energy into the fuel bed. These pulses result in highly efficient agitation of the fuel. The fuel is pneumatically mixed in lieu of a mechanical means, thereby providing efficient oxidation of the fuel. This technology uses fewer moving parts, which reduces both the equipment capital costs and the maintenance costs. Inclined fluidized bed FB grates are new and have not yet been utilized in an industrial wood-fired application, although pilot-scale testing has been successful.

See also: Combustion.

Combustion – Types of Combustors

The combustor (incinerator) is, simply, a furnace for burning refuse, and modern combustors include pollution mitigation equipment such as flue-gas cleaning. There are various types of combustor plant design: (i) simple combustor, (ii) fixed or moving grate combustor, (iii) rotary-kiln combustor, and (iv) the fluidized bed combustor.

The simple combustor is an older and simpler kind of combustor that is, essentially, a brick-lined cell with a metal grate over a lower ash pit, with one opening in the top or side for loading and another opening in the side for removing incombustible solids (clinker). Many small combustors formerly found in apartment houses have now been replaced by waste compactors.

The fixed or moving grate combustor is a fixed hearth combustor with a moving grate. The moving grate enables the movement of waste through the combustion chamber to be optimized to allow a more efficient and complete combustion. These combustors are typically used for combustion of municipal waste, and are thus referred to as MSWCs (municipal solid waste combustors).

In the fixed or moving grate combustor, the waste is introduced by a waste crane through the “throat” at one end of the grate, from where it moves down over the descending grate to the ash pit in the other end. Here, the ash is removed through a water lock. Part of the combustion air (primary combustion air) is supplied through the grate from below. This air flow also has the purpose of cooling the grate itself. Cooling is important for the mechanical strength of the grate, and many moving grates are also water-cooled internally. Secondary combustion air is supplied into the boiler at high speed through nozzles over the grate. It facilitates complete combustion of the flue gases by introducing turbulence for better mixing and by ensuring a surplus of oxygen.

The combustor must be designed to ensure that the flue gases reach a temperature of at least 850°C (1,560°F) in order to ensure proper breakdown of organic toxins. This includes backup auxiliary burners (often fueled by oil), which are fired into the boiler in case the heating value of the waste becomes too low to reach this temperature alone. The flue gas is then cooled by heat transfer and heat the steam to typically 400°C (750°F) at a pressure of 550 to 600 psi for the electricity generation in the turbine. At this point, the flue gas has a temperature of around 200°C (390°F), and is passed to the flue gas cleaning system.

In the fixed or traveling grate combustor, an automatic feeder distributes the fuel onto a grate, where the fuel burns. Combustion air enters from below the grate. In the stationary grate design, ashes fall into a pit for collection. In contrast, a traveling grate system has a moving grate that drops the ash into a hopper. In another configuration, a *pile burner* consists of separate cells and each cell consists of an upper and a lower combustion chamber for use in a step-wise burner configuration. In this type of equipment, the biomass feedstock combusted burns on a grate in the lower chamber thereby releasing volatile gases which are then combusted in the upper (secondary) combustion chamber. However, pile burners must be shut down periodically to remove the mineral ash.

The rotary kiln combustor has a primary chamber and secondary chamber. The primary chamber consists of an inclined refractory lined cylindrical tube. Movement of the cylinder on its axis facilitates movement of waste. In the primary chamber, there is conversion of solid fraction to gases, through volatilization, destructive distillation, and partial combustion reactions. The secondary chamber is necessary to complete gas phase combustion reactions.

The clinker spills out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases may be combusted in an *afterburner*. To control air pollution, the combustion product gases are further treated with acid gas scrubbers to remove sulfuric acid and emissions of nitric acid, and then routed through bag houses to remove particulate matter before the gas is released into the atmosphere.

The fluidized bed combustor uses a strong airflow through a sand bed until a point is reached where the sand particles separate to let the air through and mixing and churning occurs, thus a fluidized bed is created and fuel and waste can now be introduced. The sand with the pre-treated waste and/or fuel is kept suspended on pumped air currents and takes on a fluid-like character. The bed is thereby thoroughly mixed and agitated keeping small inert particles and air in a fluid-like state. This allows all of the mass of waste, fuel, and sand to be fully circulated through the furnace.

Fluidized-bed combustors burn biomass fuel in a hot bed of granular material, such as sand. Injection of air into the bed creates turbulence resembling a boiling liquid. The turbulence distributes and suspends the fuel. This design increases heat transfer and allows for operating temperatures up to 970°C (1,700°F), reducing nitrogen oxide (NO_x) emissions. Fluidized-bed combustors can handle high-ash fuels and agricultural biomass residue.

The heat produced by a combustor can be used to generate steam which may then be used to drive a turbine in order to produce electricity. However, the amount of energy produced is very much dependent upon the type and composition of the waste used as the feedstock. Much of the current thinking involves co-combustion of a specified amount of the waste (calculated on the basis of the carbon content of the waste) with, for example, coal to produce a consistent amount of energy. However, the combustion process has a number of outputs such as (i) the mineral ash and (ii) the emission to the atmosphere of flue gas. Before the flue gas cleaning, the flue gases may contain significant amounts of particulate matter, heavy metals, dioxin derivatives, furan derivatives, sulfur dioxide, hydrochloric acid, and polynuclear aromatic hydrocarbon derivatives (carcinogens).

The most publicized concerns related to the combustion of municipal solid wastes involve the fear that it produces significant amounts of emissions of dioxin and furan derivatives which are considered by many to be serious health hazards. Older-generation combustors that were not equipped with modern gas cleaning technologies were indeed significant sources of dioxin emissions. However, modern combustors (due to advances in emission control designs and stringent regulations) must limit and even mitigate such emissions.

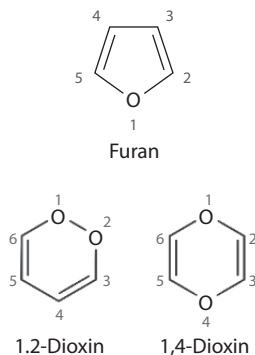
The quantity of pollutants in the flue gas from combustion plants is reduced by several processes. For example, taking an example from the gas processing industry, particulate matter is collected by particle filtration, most often electrostatic precipitators and/or baghouse filters. Hydrogen chloride and sulfur dioxide are removed in scrubbers or as in a dry desulfurization process by injection of a limestone (CaCO₃) as a slurry into the flue gas stream before the particle filtration step. Wastewater from scrubbers must subsequently pass through a wastewater treatment plant. Nitrogen oxide (NO_x) emissions are either reduced by catalytic reduction with ammonia in a catalytic converter (a selective catalytic reduction process) or by a high temperature reaction with ammonia in the furnace (a selective non-catalytic reduction process). Heavy metals are often adsorbed on injected active carbon powder (such as activated charcoal), which is collected by the particle filtration. As is the case when coal is combusted, combustion of biomass or organic waste also produces fly ash and bottom ash.

By way of explanation, heavy metals are generally defined as metals with relatively high density, atomic weight, or atomic number. Fly ash is a combustion product that is composed of the particulates (fine particles of burned fuel) that are driven out of coal-fired boilers together with the flue gases. Fly ash is, thus, that portion of the ash that escapes up the chimney or stack. On the other hand, bottom ash is part of the non-combustible residue of combustion in a power plant, boiler, furnace, or combustor. In an industrial context, it typically comprises traces of combustibles embedded in forming clinkers and sticking to hot side walls of a furnace during its operation. The clinker materials fall by themselves into the bottom hopper of a coal-burning furnace and are cooled. The above portion of the ash is also referred to as bottom ash.

The total amount of ash produced by municipal solid waste combustion ranges from 15 to 20% w/w of the waste, and the fly ash amounts to 0 to 10% w/w of the total ash. The fly ash, by far, constitutes more of a potential health hazard than does the bottom ash because the fly ash often contains high concentrations of heavy metals such as lead, cadmium, copper, and zinc as well as small amounts of dioxin derivatives and furan derivatives. The bottom ash seldom contains significant levels of heavy metals.

While fly ash is always regarded as hazardous waste, bottom ash is generally considered safe for regular landfill after a certain level of testing defined by the local legislation. Ash, which is considered hazardous, may generally only be disposed of in landfills which are carefully designed to prevent pollutants in the ash from leaching into underground aquifers – or after chemical treatment to reduce the leaching characteristics of the ash.

In spite of the promise shown by the use of combustors for waste disposal and, in some cases, energy production (in the form of fuel gases), the use of combustors for waste combustion is often controversial. On the one hand, the concerns over the health effects of the emissions of furan derivatives and dioxin derivatives have been significantly lessened by advances in emission control designs and very stringent new governmental regulations that have resulted in large reductions in the amount of dioxin derivatives and furan derivatives emissions emitted into the environment.



However, there may be concerns related to the health effects of furan and dioxin emissions into the atmosphere from old combustors. Also, combustors emit varying levels of heavy metals such as (alphabetically) arsenic, cadmium, chromium, lead manganese, mercury, nickel, and vanadium, which can be toxic at very minute levels. Other advanced alternative technologies are available such as biological treatment combined with anaerobic digestion and gasification.

Combustion Zone

The combustion zone is where the area feedstock occurs. However, the process that occurs in the combustion zone is not always as straightforward as simple equations indicate.

Combustion, with rare exceptions, is a complex chemical process involving many steps that depend on the properties of the combustible substance. It is initiated by external factors such as heat, light, and sparks. The reaction sets in as the mixture of combustibles attains the ignition temperature. The combustion spreads from the ignition source to the adjacent layer of gas mixture. In fact, each point of the burning layer serves as an ignition source for the next adjacent layer. Combustion terminates when an equilibrium is achieved between the total heat energies of the reactants and the total heat energies of the products. Most reactions terminate when what is called thermal equilibrium has been attained when the energy of the reactants equals the energy of the products.

See also: Combustion.

Combustion Plants

Modern combustion plants generate electricity and heat that can be sold to the regional electric grid and can sell steam to district heating systems or industrial customers. The bottom ash residue remaining after combustion has been shown to be a non-hazardous solid waste that can be safely landfilled or possibly reused. In densely populated areas, finding space for additional landfills is becoming increasingly difficult.

Combustion of municipal solid waste avoids the release of carbon dioxide and methane. Every ton of municipal solid waste incinerated, prevents approximately one ton of carbon dioxide equivalents from being released to

the atmosphere. Combustion of medical waste and sewage sludge produces an end product ash that is sterile and non-hazardous. On the other hand, the end product ash must still be safely sent for disposal. Many countries deny the use of combustion as an option for the treatment of their municipal solid wastes because of the potential of environmental pollution. In addition, combustors produce soot particles ($PM_{2.5}$, nanoparticles, i.e., particles with a size less than 2.5 microns, $<1 \times 10^{-6}$ meter) in the furnace. Even with modern particle filtering of the flue gases – such as baghouse filters – some of these small particles are emitted to the atmosphere.

In summary, combustion is not a complete method of disposal; its main advantage is that it produces a residue that is substantially reduced in volume and may be relatively inert. In addition, the efficiency of a combustor is, on occasion, due to excessive throughput or choice of operating parameters that are less than desired. For example, the operating temperature inside the plant should be at the specified temperature (usually on the order of 850°C, 1,560°F) to reduce the possible effects of the most dangerous air pollutants and the production of dioxins. A lower than specified combustion temperature implies incomplete combustion, leaving part of the waste in the ashes and other combustion residues. Furthermore, the exhaust gases may be unnecessarily polluting because of the low combustion temperature and the by-products of such combustion may be sent to an unprotected landfill for disposal.

Combustion plants are usually classified as mass burn systems or refuse-derived fuel (RDF) systems. In the mass burn system, all waste is incinerated; they are large facilities, over 200 tons (4,000 lbs) per day. Most mass burn systems burn waste in a single combustion chamber with excess air. The waste is burned on a sloping moving grate which helps agitate the municipal solid waste and mixes the waste with combustion air; many different proprietary grate systems exist. Grate design is critical because it must agitate the waste sufficiently to provide complete combustion and minimize ash carry-over in the flue gas which contributes to emissions.

In the boiler/furnace portion of the combustor, the waste characteristics of interest are the calorific value, moisture content, proportion of non-combustibles, and other components such as heavy metals, chlorine, and sulfur whose presence during combustion will result in the need for flue gas cleanup. The capacity of the furnace/boiler of the combustor is approximately proportional to the calorific value of the waste. Mass burn produces by-products which have damaging consequences on the environment. Pollution control systems can be used to mitigate such risks. The technologies used to recover energy from municipal solid waste include (i) waterwall combustion and (ii) modular combustion.

Waterwall combustion involves the combustion of unprocessed municipal solid waste (mass burning) or processed municipal solid waste in a furnace with integral boiler tubes. Waterwall units have been built as small as 75 to 100 tons per day capacity. However, the cost per ton of rated capacity of such units is relatively high. A more common unit size is 250 to 300 tons per day, while waterwall mass-fired units have been built as large as 750 to 1,200 tons per day capacity.

The advantages of waterwall combustion are (i) pre-processing of waste is not required, except for large bulky items; (ii) the ash produced could be used for block manufacture; and (iii) auxiliary fuel is not required during normal steady-state operation. On the other hand, the challenges of water wall combustion are (i) capital and operating costs are high, (ii) complexity of operation, control, and maintenance; and (iii) reserve furnace capacity is not available during downtime. Modular combustion is used in smaller plants and is an assembly of prefabricated major components assembled in the field to form a total operation. Modular combustors have been built in individual unit sizes up to 100 tons per day, combined into plants of just over 400 tons per day.

Modular systems are similar to mass burn systems in that these systems not only combust unprocessed municipal solid waste but also feature two combustion chambers, and the municipal solid waste is charged into the system by a hydraulic ram and combustion takes place on a series of stationary hearths. The municipal solid waste is pushed from one hearth to the next by hydraulic rams. Two types of modular systems have been built and operated: starved air (slightly oxygen deficient) and excess air (greater than stoichiometric).

The advantages of modular combustion are low cost and shorter field construction time given their modular construction. The disadvantages of modular combustion are waste burnout is not always complete (increased ash quantities and reduced energy recovery); combustion control is less effective (possibility of discharge of trace organics); lower quality of equipment; and less redundancy than larger mass-fired water wall and refuse-derived fuel waste to energy plants.

Feedstock preparation plays an important role in any thermal waste conversion approach. Refuse-derived fuel (RDF) is produced when municipal solid waste is processed by mechanical means [picking, separation of inert

materials (glass, minerals, ferrous and non-ferrous metals), flailing, screening, shredding, and conditioning] to produce a more homogenous material prior to combustion. RDF systems utilize pre-treated municipal solid waste. Several types of RDF are generated – coarse, fluff, powder, densified – which differ in complexity, power requirements, particle size and whether the material is compacted into pellets or briquettes. RDF can be used as the primary fuel source in a dedicated boiler or co-fired with a conventional fossil fuel as natural gas or landfill gas. The heating value of nearly all solid waste fuels is a function of carbon content. Ash content is generally low, but the amount of moisture is highly variable and depends upon moisture generation plus the effects of processing, handling, and storage.

Scrap tires can be processed into a waste-derived fuel (WDF) and mixed with other fuels without major alteration to the existing combustion facility. Tire-derived fuels (TDFs) are commonly used as supplemental fuel in cement kilns which are technologically and environmentally superior for selective waste disposal due to favorable internal kiln conditions as flame temperature (1,850°C, 3,360°F), residence time, alkaline environment, high gas turbulence, and mixing which ensure complete combustion, and the added benefit of having no bottom ash disposal problem since the residual materials (e.g., steel from steel-belted tires) are incorporated into the clinker. The rationale behind the use of tire-derived fuel is as follows: (i) excellent combustion characteristics and high heating value, HHV, (ii) lower cost and good availability, (iii) relatively low sulfur content, especially on a Btu basis, and (iv) a reduction in the environmental burden and health effects of tire stockpiles.

Typically, the sulfur content of scrap tires and TDFs is on the order of 1.5 to 2.0% w/w. Considering the emission potential of sulfur dioxide per the generated energy value of the fuel, the result is closer to that for low sulfur-containing coals.

Complete Mix Digester

A complete mix digester converts organic waste to biogas in a heated tank above or below ground. A mechanical or gas mixer keeps the solids in suspension. Complete mix digesters are expensive to construct and cost more than plug-flow digesters to operate and maintain.

Complete mix digesters are suitable for larger manure volumes having solids concentration of 3 to 10%. The reactor is a circular steel or poured concrete container. During the digestion process, the manure slurry is continuously mixed to keep the solids in suspension. Biogas accumulates at the top of the digester. The biogas can be used as fuel for an engine-generator to produce electricity or as boiler fuel to produce steam. Using waste heat from the engine or boiler to warm the slurry in the digester reduces retention time to less than 20 days.

See also: Aerobic Digestion, Anaerobic Digestion, Digester.

Concentrated Acid Hydrolysis

This process is based on concentrated acid decrystallization of cellulose followed by dilute acid hydrolysis to sugars at near theoretical yields. Separation of acid from sugars, acid recovery, and acid reconcentration are critical unit operations. Fermentation converts sugars to ethanol.

The heart of the process is the decrystallization followed by dilute acid hydrolysis. The original Peoria process, developed by USDA researchers in World War II, and a modified version proposed by Purdue, carry out dilute acid pretreatment to separate the hemicellulose before decrystallization. The biomass would then be dried to concentrate the acid absorbed in the biomass prior to addition of concentrated sulfuric acid. Purdue proposed recycling sulfuric acid by taking the dilute acid/water stream from the hydrolysis reactor and using it in the hemicellulose pretreatment step.

In the Arkenol process, decrystallization is carried out by adding 70% to 77% sulfuric acid to biomass that has been dried to 10% moisture. Acid is added at a ratio of 1.25:1 (acid: cellulose + hemicellulose), and temperature is controlled at less than 50°C (122°F). Adding water to dilute the acid to 20% to 30% and heating at 100°C (212°F) for an hour results in the release of sugars. The gel from this reactor is pressed to remove an acid/sugar product stream. Residual solids are subjected to a second hydrolysis step. The use of a chromatographic column to achieve a high yield and separation of acid and sugar is a crucial improvement in the process. The fermentation converts both the

xylose and the glucose to ethanol at theoretical yields of 85% and 92%, respectively. A triple effect evaporator is required to reconcentrate the acid.

See also: Acid Hydrolysis, Hydrolysis – Lignocellulosic Materials.

Condensation

Condensation occurs when the air becomes saturated with moisture (relative humidity = 100%). As the temperature falls, the relative humidity of the air rises – the temperature at which condensation begins is the dew point. Condensation typically occurs on preexisting surfaces such as dust particles and aerosols to form tiny cloud droplets. The droplets are readily kept airborne by air turbulence until they become so common. As the droplets collide and coalesce, the larger droplets fall, colliding with other droplets to eventually form a raindrop (containing approximately one million cloud droplets). With decreasing temperatures (less than -10°C , 14°F), ice crystals replace water droplets.

The phase change that accompanies water as it moves between the vapor, liquid, and solid forms is exhibited in the arrangement of water molecules, which are arranged more randomly than in liquid water. As condensation occurs and liquid water forms from the vapor, the water molecules become more organized and heat is released into the atmosphere.

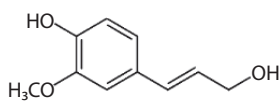
Even though clouds are absent in a crystal-clear blue sky, water is still present in the form of water vapor and droplets which are too small to be seen. Depending on weather conditions, water molecules will combine with tiny particles of dust, salt, and smoke in the air to form cloud droplets, which combine and grow and develop into clouds, a form of water we can see. Cloud droplets can vary greatly in size, from 10 microns (millionths of a meter) to 1 millimeter (mm), and even as large as 5 mm. This process occurs higher in the sky where the air is cooler and more condensation occurs relative to evaporation. As water droplets combine (also known as coalescence) with each other, and grow in size, clouds not only develop, but precipitation may also occur. Precipitation is essentially water in its liquid or solid form falling from the base of a cloud. This seems to happen too often during picnics or when large groups of people gather at swimming pools.

The clouds formed by condensation are an intricate and critical component of Earth's environment. Clouds regulate the flow of radiant energy into and out of Earth's climate system. They influence the Earth's climate by reflecting incoming solar radiation (heat) back to space and outgoing radiation (terrestrial) from the Earth's surface. Often at night, clouds act as a "blanket," keeping a portion of the day's heat next to the surface. Changing cloud patterns modify the Earth's energy balance, and, in turn, temperatures on the surface of the Earth.

See also: Atmosphere, Water Cycle.

Coniferyl Alcohol

Coniferyl alcohol is a colorless crystalline organic compound that occurs in gymnosperm and angiosperm plants. Sinapyl alcohol and paracoumaryl alcohol – the two other lignin isomers – are found in angiosperm plants and grasses.



Coniferyl alcohol

Coniferyl alcohol is a phytochemical that is synthesized via the phenylpropanoid biochemical pathways. When copolymerized with related aromatic compounds, coniferyl alcohol forms lignin and lignans.

In softwood species, coniferyl alcohol is the dominant monomer (94% coniferyl, 1% sinapyl, 5% coumaryl alcohols). In hardwood species, both coniferyl alcohol and sinapyl alcohols are present in significant amounts, whereas grasses have large quantities of all three phenyl propylene derivatives.

See also: Hardwood, Grasses, Lignin, Sinapyl Alcohol, Softwood, Paracoumaryl Alcohol.

Conservation

The term conservation refers to the more efficient use of the existing natural resources. Clearly, maximizing conservation is an important and worthwhile contribution to help alleviate existing and future energy problems. Although substantial efforts have already been made toward improving conservation, there are still many more opportunities that have yet to be exploited.

There are two ways by which conservation can be implemented, one of which has a good chance of acceptance by the public and the other which is on much shakier ground. Although both approaches conserve energy, they are separated by a relatively clear line in the sand. The attractive approach takes advantage of advances in technology to conserve fuel while maintaining performance in appliances, automobiles, and other equipment used in daily living. Examples of this approach include hybrid automobiles, more efficient appliances, and additional insulation for older homes.

The second and more difficult approach to conservation requires that citizens directly reduce their use of energy in certain aspects of their daily living. Often, this is viewed as a reduction in standard of living. The public is in general much more reluctant to give up something to which they are already accustomed. Examples of this approach to conservation include smaller, more gasoline-efficient automobiles, smaller houses, increased use of public transportation, less use of air conditioning in summer, and lower thermostat settings in the winter.

With the continually increasing demand for new electricity, particularly by some of the developing nations, it is difficult to imagine that conservation can completely solve the world's future electricity generation problems. Nevertheless, it can reduce the magnitude of the problems. This would afford the nations of the world more time to develop and transition to new alternatives.

See also: Conservation Reserve Program

Conservation Reserve Program

The conservation reserve program (CRP) provides farm owners or operators with an annual per-acre rental payment and half the cost of establishing a permanent land covers in exchange for retiring environmentally sensitive cropland from production for 10 to 15 years. In 1996, Congress reauthorized CRP for an additional round of contracts, limiting enrollment to 36.4 million acres at any time.

The 2002 Farm Act increased the enrollment limit to 39 million acres. Producers can offer land for competitive bidding based on an Environmental Benefits Index (EBI) during periodic signups, or can automatically enroll more limited acreages in practices such as riparian buffers, field windbreaks, and grass strips on a continuous basis. CRP is funded through the Commodity Credit Corporation (CCC).

Contaminant

A contaminant, which is not usually classified as a pollutant unless it has some detrimental effect, can cause deviation from the normal composition of an environment. On the other hand, a receptor is an object (animal, vegetable, or mineral) or a locale that is affected by the pollutant.

In environmental chemistry, the term contaminant is, in some cases, used to be equivalent to pollutant, where the main interest is the harm done on a large scale to humans, organisms, or environments. An environmental contaminant may be chemical in nature, though it may also be a biological (such as pathogenic bacteria, virus, and invasive species) or physical (energy) agent.

See also Pollutant.

Contingent Resources

Contingent resources (sometimes referred to as probable resources or possible resources) are those quantities of crude oil that are estimated, on a given date, to be potentially recoverable from known accumulations, but which are not considered as commercially recoverable (Table C-9).

Table C-9 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered			
		Nonrecoverable		
		Recoverable		
			Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Some ambiguity may exist between the definitions of contingent resources and unproved reserves. This is a reflection of variations in current industry practice, but if the degree of commitment is not such that the accumulation is expected to be developed and placed on production within a reasonable time frame, the estimated recoverable volumes for the accumulation can be classified as contingent resources. Contingent resources may include, for example, accumulations for which there is currently no viable market, or where commercial recovery is dependent on the development of new technology, or where evaluation of the accumulation is still at an early stage.

Conventional Fuel Sources

Crude oil is recognized as the prominent conventional fuel source. Thus, in the context of the definition of a renewable fuel or synthetic fuel that is defined in the context of substitutes for crude oil-based fuel (q.v.), the term conventional fuel implies any available fuel derived from crude oil.

Crude oil and the equivalent term crude oil cover a vast assortment of materials that consist of gaseous, liquid, and solid hydrocarbon-type chemical compounds that occur in sedimentary deposits throughout the world. When crude oil occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark-to -light-colored liquid, it is often referred to as conventional crude oil.

The United States Congress has defined tar sands as several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques. By inference, heavy oil, which can be recovered in its natural state by conventional oil well production methods including currently used enhanced recovery techniques, does not fall into the same category as tar sand bitumen and therefore is a type of crude oil. Thus, heavy oil is a type of crude oil that is different from conventional crude oil insofar the flow properties are reduced and a heavy oil is much more difficult to recover from the subsurface reservoir. These materials have a high viscosity (and low API gravity) relative to the viscosity (and API gravity) of conventional crude oil, and recovery of heavy oil usually requires thermal stimulation of the reservoir.

The definition of heavy oil is usually based on the API gravity or viscosity, but the definition is quite arbitrary. Although there have been attempts to rationalize the definition based upon viscosity, API gravity, and density, such definitions based on physical properties are inadequate and a more precise definition should involve some reference to the recovery method.

However, in a very general sense (and not in any sense meant to indicate classification of heavy oil), the term heavy oil is often applied to a crude oil that has a gravity $<20^\circ$ API and usually, but not always, a sulfur content higher than 2% w/w. Furthermore, in contrast to conventional crude oil, heavy oil is darker in color and may even be black. The term heavy oil has also been arbitrarily used to describe the heavy oil that requires thermal stimulation of

recovery from the reservoir and (albeit incorrectly) the bitumen in bituminous sand (tar sand, oil sand) formations from which the highly viscous bituminous material is recovered by a mining operation.

Crude oil varies widely in composition, and variations of the composition of heavy oil add further complexity to the use of these feedstocks in the production of liquid fuels. The variations in composition are generally reflected in variations in the API gravity, viscosity, and the potential for coke formation in thermal process, to mention only three of the affected properties. In addition to the organic constituents, there are also metal-containing constituents (notably those compounds that contain vanadium and nickel) which usually occur in the more viscous crude oil in amounts up to several hundred parts per million.

Physical methods of fractionation of crude oil and heavy oil can be achieved to produce four bulk generic fractions: saturates aromatics, resins, and asphaltenes. The relative amounts of these fractions have often been equated to the behavior of crude oil or heavy oil feedstocks during recovery and refining.

Conversion Pathways

Energy conversion of organic materials can proceed along three main pathways: (i) thermochemical conversion, (ii) biochemical conversion, and (iii) physicochemical conversion. Currently, all three pathways are utilized to varying degrees with fossil fuel feedstocks.

Thermochemical conversion processes include the typical processes such as combustion, gasification, and pyrolysis.

Biochemical conversion processes include aerobic conversion (i.e., composting), anaerobic decomposition or digestion (which occurs in landfills and controlled reactors or digesters), and anaerobic fermentation (for example, the conversion of sugars from hydrolyzed cellulose and hemicellulose by ethanol-producing yeasts and recombinant bacteria. Physicochemical conversion involves the physical and chemical synthesis of products from feedstocks (for example, biodiesel).

Biochemical conversion proceeds at lower temperatures and lower reaction rates. Higher moisture feedstocks are generally good candidates for biochemical processes. Thermochemical conversion is characterized by higher temperatures and faster conversion rates. It is best suited for lower moisture feedstocks. For biomass feedstocks, the lignin fraction currently cannot be converted biochemically, although research is investigating lignin fermentation processes. On the other hand, thermochemical routes can convert the entire organic portion of suitable feedstocks. The inorganic fraction (ash) of a feedstock does not contribute significantly to the energy products but does participate in important ways including fouling of high temperature equipment, increased nutrient (e.g., K and P) loading in facility wastewater treatment and disposal, and in some cases by providing marketable co-products or adding disposal cost. Inorganic constituents may also be catalytic for some of the conversion reactions.

Physicochemical conversion involves the physical and chemical synthesis of products from feedstocks and is primarily associated with the transformation of fresh or used vegetable oils, animal fats, greases, tallow, and other suitable feedstocks into liquid fuels or biodiesel.

See also: Conversion Processes, Biochemical Platform, Thermochemical Platform.

Conversion Processes – Biochemical

Biochemical conversion of biomass is completed through alcoholic fermentation to produce liquid fuels and anaerobic digestion or fermentation, resulting in biogas. Alcoholic fermentation of crops such as sugarcane and maize (corn) to produce ethanol for use in internal combustion engines has been practiced for years with the greatest production occurring in Brazil and the United States, where ethanol has been blended with gasoline for use in automobiles. With slight engine modifications, automobiles can operate on ethanol alone.

Anaerobic digestion of biomass has been practiced for almost a century, and is popular in many developing countries such as China and India. The organic fraction of almost any form of biomass, including sewage sludge, animal wastes, and industrial effluents, can be broken down through anaerobic digestion into methane and carbon dioxide.

This biogas is a reasonably clean burning fuel which can be captured and put to many different end uses such as cooking, heating, or electrical generation.

Fermentation plants producing biogas are in routine use, ranging from farms to large municipal plants. As feedstock, they use manure, agricultural residues, urban sewage, and waste from households, and the output gas is typically 64% methane. The biomass conversion process is accomplished by a large number of different agents, from the microbes decomposing and hydrolyzing plant material, over the acidophilic bacteria dissolving the biomass in aquatic solution, and to the strictly anaerobic methane bacteria responsible for the gas formation. Operating a biogas plant for a period of some months usually makes the bacterial composition stabilize in a way suitable for obtaining high conversion.

The photosynthetic production of gas (e.g., hydrogen) employs microorganisms such as cyanobacteria, which have been genetically modified to produce pure hydrogen rather than the metabolically relevant substances. The conversion efficiency from sunlight to hydrogen is small, usually under 0.1%, indicating the need for large collection areas.

If the bacteria are modified to produce maximum hydrogen, their own growth and reproduction are quenched. Presumably, there has to be made a compromise between the requirements of the organism and the amount of hydrogen produced for export, so that replacement of organisms (produced at some central biofactory) does not have to be made at frequent intervals. The implication of this is probably an overall efficiency lower than 0.05%.

See also: Aerobic Digester, Anaerobic Digester, Digesters.

Conversion Processes – Biomass Properties

Each type of biomass has its own specific properties which determine performance as a feedstock in gasification plants. The most important properties relating to gasification are (i) moisture content, (ii) mineral content leading to ash production, (iii) elemental composition, (iv) bulk density and morphology, and (v) volatile matter content.

The moisture content of biomass is defined as the quantity of water in the material expressed as a percentage of the weight of the material. For processes like gasification, preference is given to relative dry biomass feedstocks because a higher-quality gas is produced, i.e., higher heating value, higher efficiency, and lower tar levels. Natural drying is cheap but requires long drying times. Artificial drying is more expensive but also more effective. In practice, artificial drying is often integrated with the gasification plant to ensure a feedstock of constant moisture content. Waste heat from the engine or exhaust can be used to dry the feedstock.

Ash content (which represents an inorganic content) of biomass is the inorganic oxides that remain after complete combustion of the feedstock. The amount of ash between different types of feedstocks differs widely (0.1% for wood up to 15% for some agricultural products) and influences the design of the reactor, particularly the ash removal system. The chemical composition of the ash is also important because it affects the melting behavior of the ash. Ash melting can cause slagging and channel formation in the reactor. Slag can ultimately block the entire reactor.

The elemental composition of the biomass feedstock is important with regard to the heating value of the gas and to the emission levels. The production of nitrogen and sulfur compounds is generally small in biomass gasification because of the low nitrogen and sulfur content in biomass.

The bulk density refers to the weight of material per unit of volume and differs widely between different types of biomass. Together with the heating value, it determines the energy density of the gasifier feedstock, i.e. the potential energy available per unit volume of the feedstock. Biomass of low bulk density is expensive to handle, transport, and store. Apart from handling and storing behavior, the bulk density is important for the performance of the biomass as a fuel inside the reactor: a high void space tends to result in channeling, bridging, incomplete conversion, and a decrease in the capacity of the gasifier. The bulk density varies widely (100 to 1,000 kg/m³) between different biomass feedstocks not only because of the character of the biomass but also as a result of the way the biomass comes available (chips, loose, baled).

The amount of volatile products (volatile matter content) has a major impact on the tar production levels in gasifiers. Depending on the gasifier design, the volatile matter leaves the reactor at low temperatures (updraft gasifiers) or passes through a hot incandescent oxidation zone (downdraft gasifiers) where it is thermally cracked. For biomass materials, the volatile matter content varies between 50 and 80%.

Feedstock preparation is required for almost all types of biomass materials because of large variety in physical, chemical, and morphological characteristics. The degree to which any specific pretreatment is desirable will depend upon the gasifier. For example, capacity and type of reactor (downdraft gasifiers are stricter to uniform fuel specifications than updraft gasifiers) are important aspects of biomass gasification.

Sizing of the feedstock may be necessary as different sizes are specified for different types of gasifiers. For small-scale fixed bed gasifiers, cutting and/or sawing of wood blocks is the preferred form of fuel preparation. Chipped wood is preferred for larger-scale applications. The size range of chips can be chosen by screening such that the fuel is acceptable for a specific gasifier type. For medium- and large-scale fixed bed gasifiers, wood chips from forestry or wood processing industries are produced by crushers, hammer mills, shredders, and/or mobile chippers (particularly for thinnings from landscape conservation activities). Most of these sizing apparatus are provided with a screen. Dependent on the feedstock morphology and characteristics (hardness), the throughput or capacity varies considerably.

Drying of the biomass fuel is advisable if fresh wet materials (moisture content 50-60% on wet basis) are to be gasified. Lowering the moisture content of the feedstock is associated with a better performance of the gasifier. Utilizing the exhaust gases from an internal combustion engine is a very efficient way to do so. The sensible heat in engine exhaust is sufficient to dry biomass from 70% down to 10%. Rotary kilns are the most applied dryers. The energy costs of drying are high, but these can be outweighed by the lower downstream gas cleaning requirements for dried feed.

Densification, such as briquetting or pelletization, is an important technique to densify biomass materials for increasing the particle size and bulk density. The reasons for biomass include (i) densified biomass is less expensive to transport, (ii) densified products are easier to store and handle, and (iii) densification enables certain biomass feedstocks to be gasified in a specific gasifier.

The calorific value of the gas is the prime factor for power generation – the higher the value, the better. Hence, the availability in the gas of any compounds that increase calorific value is generally welcomed – product gas, which contains carbon monoxide (CO), hydrogen (H_2), and various hydrocarbon derivatives [methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6), tars, and chars]. The presence of inert components [water (H_2O), carbon dioxide (CO_2), and nitrogen (N_2)] is also acceptable, provided it is kept within certain limits.

Environmental concerns include disposal of associated tars and ashes, particularly for the fluidized bed reactors, where these substances must be separated from the flue gas stream (in contrast to the pyrolysis plants, where most tar and ash deposit at the bottom of the reactor). Concerns over biomass transportation are similar to those mentioned above for fermentation, and a positive fertilizer effect can also in many cases be derived from the gasification residues.

Biomass ash also has the potential to be used as a clarifying agent in water treatment, as a wastewater adsorbent, as a liquid waste adsorbent, as a hazardous waste solidification agent, as a lightweight fill for roadways, parking areas, and structures, as asphalt mineral filler, or as a mine spoil amendment.

Conversion Processes – Combustion

Combustion offers the most direct route for energy recovery, and is an effective means of utilizing the total energy content of whole wood and other biomass. Technology for the combustion of carbonaceous feedstocks is well developed and feasible.

Gasification results in only a partial oxidation of the carbon constituent. Much of the calorific value of the original fuel leaves the gasifier in the form of chemical energy in carbon monoxide, methane, and hydrogen.

In combustion, air containing sufficient oxygen to completely oxidize the hydrocarbon is used. The resulting gas (flue gas) is essentially all carbon dioxide, water vapor, and diluent nitrogen, and has no calorific value. The energy of the original fuel leaves the system as sensible heat that can be used for steam generation and, if required, electricity generation.

Thus, combustion offers a practical means for recovering the energy in biomass materials, using currently available technology.

However, due to the large land area over which biomass must be harvested, the seasonal nature of the supply, and the large volume of material to be transported and stored, the reliable provision of biomass to a large combustion plant can present considerable problems.

See also: Combustion, Combustion – Chemistry, Combustion – Effect of Additives and Catalysts, Combustion – Environmental Aspects, Combustion – Fluidized Bed, Combustion – Fouling, Combustion – Fouling – Heat Balance, Combustion – Ignition, Combustion – Influence of Feedstock Quality, Combustion – Mechanism, Combustion – Soot Formation, Combustion – Surface Effects.

Conversion Processes – Gasification

Gasification, a thermal conversion process, occurs through the thermal decomposition of biomass with the help of an oxidant such as pure oxygen or oxygen-enriched air to yield a combustible gas such as synthesis gas rich in carbon monoxide and hydrogen. The synthesis gas is post-treated, by steam reforming or partial oxidation, to convert the hydrocarbon derivatives produced by gasification into hydrogen and carbon monoxide. The carbon monoxide is then put through the shift process to obtain a higher fraction of hydrogen, by carbon dioxide removal and methanation or by pressure swing adsorption.

In the gasification process, one or more reactants, such as oxygen, steam, or hydrogen, are introduced into the system. These chemical reactants combine with solid carbon at the higher gasification temperatures, so increasing the gas yield while consuming char. The amount of char by-product remaining on gasification is in fact essentially zero with biomass materials, while the small quantity of tars and oils evolved may be recycled to extinction. The introduced reactants also enter into gas phase reactions which, together with the shift in equilibrium and the change in relative reaction rates at the higher temperatures, results in a significantly better-quality gas than that obtained on pyrolysis. Important distinctions between pyrolysis and gasification are therefore the improved gas yield and the elimination of solid and liquid by-products.

One major advantage with gasification is the wide range of biomass resources available, ranging from agricultural crops, and dedicated energy crops to residues and organic wastes. The feedstock might have a highly various quality, but still the produced gas is quite standardized and produces a homogeneous product. This makes it possible to choose the feedstock that is the most available and economic at all times.

The air-blown direct gasifiers operated at atmospheric pressure and used in power generation – fixed bed updraft and downdraft and fluidized bed bubbling and circulating – are not suitable for biomass-to-liquids production. In addition, downdraft fixed bed gasifiers face severe constraints in scaling and are fuel inflexible, being able to process only fuels with well-defined properties. Updraft fixed bed gasifiers have fewer restrictions in scaling, but the produced gas contains a lot of tars and methane.

Fluidized bed gasifiers generally do not encounter limitations in scaling and are more flexible concerning the particle size of fuels. Nevertheless, they still have limited fuel flexibility, due to a risk of slagging and fouling, agglomeration of bed material, and corrosion. The operating temperatures of air-blown fluidized bed gasifiers are therefore kept relatively low (800 to 1,000°C, 1,470 to 1,830°F), which implies incomplete decomposition of feedstocks, unless long residence times are used. Fluidized bed gasifiers (especially the bubbling bed ones) tend to contaminate the product gas with dust. The oxygen-blown atmospheric or pressurized circulating fluidized bed gasifiers and the steam-blown gas or char indirect gasifiers are better solutions for biomass-to-liquids production. Both gasifying concepts significantly reduce the amount of nitrogen in the product gas. In the first case, it is achieved via substituting air with oxygen. In the second case, nitrogen ends up in the flue gas, but not in the product gas, because gasification and combustion are separated – the energy for the gasification is obtained by burning the chars from the first gasifier in a second reactor.

The gasification of biomass (such as, e.g., wood scrap) is a well-known process, taking place in pyrolysis (oxygen supply far below what is required for complete combustion, the fraction called equivalence ratio) or fluidized-bed type of reactors. Conditions such as operating temperature determine whether hydrogen is consumed or produced in the process. Hydrogen evolution is largest for near-zero equivalence ratios, but the energy conversion efficiency is highest at an equivalence ratio around 0.25. The hydrogen fraction (in this case typically some 30%) must be separated for most fuel-cell applications, as well as for long-distance pipeline-transmission. In the pyrolysis-type application, gas production is low and most energy is in the oily substances that must be subsequently reformed in order to produce significant amounts of hydrogen. Typical operating temperatures are around 850°C. An overall energy conversion efficiency of around 50% is attainable, with considerable variations. Alternate concepts use membranes

to separate the gases produced, and many reactor types use catalysts to help the processes to proceed in the desired direction, notably at a lower temperature (down to some 500°C, 930°F).

See also: Gasification of Biomass.

Conversion Processes - Pyrolysis

Pyrolysis is the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion.

Pyrolysis dates back to at least ancient Egyptian times when tar for caulking boats and certain embalming agents were made by pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly.

Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon-rich gas mixture, an oil-like liquid, and a carbon-rich solid residue. The pyrolysis of treatment of biomass to produce hydrocarbon derivatives has been studied since the 1930s, and while relatively simple to perform, typically, such processes are non-selective, producing a wide range of products. Thus, direct thermochemical conversion processes including pyrolysis to produce fuels from biomass are also possible resulting in the production of gaseous products (gaseous fuels), liquid products (liquid fuels), and charcoal (solid fuels).

The pyrolysis of biomass is a thermal treatment that results in the production of charcoal, liquid, and gaseous products. Thus, biomass is heated in the absence of air and breaks down into a complex mixture of liquids, gases, and a residual char. If wood is used as the feedstock, the residual char is what is commonly known as charcoal. With more modern technologies, pyrolysis can be carried out under a variety of conditions to capture all the components, and to maximize the output of the desired product be it char, liquid, or gas.

The liquid fraction of the pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase were higher than those of the non-aqueous phase. The point where the cost of producing energy from fossil fuels exceeds the cost of biomass fuels has been reached. With few exceptions, energy from fossil fuels will cost more money than the same amount of energy supplied through biomass conversion.

Wood contains 80% or more of volatile organic matter that may be recovered as a gas and tar on pyrolysis. Pyrolysis of wood was at one time used for obtaining creosote oils as well as acetic acid (wood vinegar) and some methanol (wood spirits). The gases evolved (hydrogen, methane, carbon monoxide, and carbon dioxide) had no value for illumination purposes and were used to supply the heat for the pyrolysis. Gasification of wood may be used to produce either a low- or a medium-heat content gas if a gaseous fuel is desired, or a synthesis gas that can be converted to liquid fuels using one of the indirect liquefaction processes. Gasification followed by a synthesis step is expected to yield a higher-quality liquid than can be obtained by pyrolysis.

The relative quantity of char, tars, and gases evolved on pyrolysis is strongly dependent on the feedstock, then on the rate of heating and the final temperature attained. Slow-heating, low temperature pyrolysis favors char yields. After the initial decomposition, subsequent coking and cracking reactions can result in a char that contains oxygen and hydrogen in addition to the carbon.

Apart from char and water, some tars and gases are always produced. The watery distillate evolved from wood at 160 to 175°C (320 to 345°F) is called pyroligneous acid and contains 5 to 10% acetic acid and 1.5 to 3% methanol. This used to be the source of methanol when it was produced by the destructive distillation (pyrolysis) of wood.

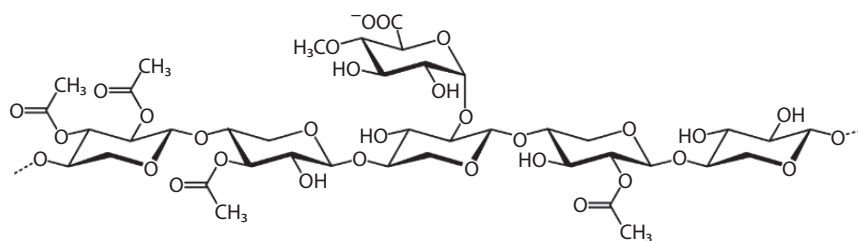
The higher boiling tar fraction produced at higher temperatures is more important as a source of liquid fuels. It contains aromatic hydrocarbon derivatives and creosote oil evolved from the lignin, as well as aliphatic compounds. The creosote oil, which consists of high-molecular-weight phenols, used to be considered the most valuable constituent of the tar fraction, in part due to its potential for resin manufacture. As a whole, the tar fraction is a viscous, highly oxygenated oil that is unstable and corrosive.

The pyrolysis option for biomass is attractive because solid biomass and wastes can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing.

The mechanism of the pyrolysis of biomass is proposed to involve heat variations, associated with the thermal degradation reactions, which affect the pyrolysis route. Several endothermic and/or exothermic peaks for biomass pyrolysis are indicated. Accordingly, cellulose pyrolysis is endothermic but lignin pyrolysis is exothermic.

However, the pyrolysis of biomass is more complex than originally believed and the general changes that occur during biomass pyrolysis are: (i) heat transfer from a heat source, to increase the temperature inside the fuel, (ii) the initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char, (iii) the flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel, (iv) condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar, (v) autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition, and (vi) further thermal decomposition, reforming, water gas shift reactions, radical recombination, and dehydrations can also occur, which are a function of the residence time/temperature/pressure profile of the process.

The chemical structure of xylan is variable, but for the xylan in hardwood, the structure can be shown as:



Also, the pyrolysis of the pyroligneous acid produces 50% methanol, 18% acetone, 7% esters, 6% aldehydes, 0.5% ethyl alcohol, 18.5% water, and small amounts of furfural. The composition of the water-soluble products was not ascertained but it has been reported to be composed of hydrolysis and oxidation products of glucose such as acetic acid, acetone, simple alcohols, aldehydes, and sugars.

See also: Pyrolysis.

Conversion Processes – Thermal

In keeping with crude oil refining technology, conversion processes as used in the biofuels industry change the size and/or structure of feedstock constituents.

Biomass conversion is accomplished through the use of several distinct processes which include both biochemical conversion and thermal conversion to produce gaseous, liquid, and solid fuels which have high energy contents, are easily transportable, and are therefore suitable for use as commercial fuels.

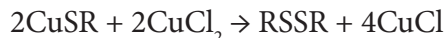
Thermal conversion offers an effective means for the recovery or conversion of the energy content of wood and other lignocellulosic biomass. Wood and many other similar types of biomass which contain lignin and cellulose (agricultural wastes, cotton gin waste, wood wastes, peanut hulls etc.) can be converted through thermochemical processes into solid, liquid, or gaseous fuels. Pyrolysis, used to produce charcoal since the dawn of civilization, is still the most common thermochemical conversion of biomass to commercial fuel.

Direct conversion processes, i.e., combustion, of biomass encounters the same problems as those in case of coal or other solid fuels. The conversion of biomass into other useful forms such as synthetic gas or liquid fuels is considered as an alternative way to make use of biomass energy. Gasification is an effective and well-known technology which has been applied to coal, but the technology developed for coal is not exactly suited to biomass utilization because of the different physical and chemical properties between coal and biomass.

See also: Thermal Conversion, Thermal Decomposition, Thermochemical Platform.

Copper Sweetening Process

The copper sweetening process is a process for the purification of liquid fuels which involves oxidation of mercaptans to disulfides by oxygen in the presence of cupric chloride. The oxidizing power of cupric (Cu^{2+}) salts is also utilized to convert mercaptans directly into disulfides; free sulfur is not employed, and polysulfides are not obtained. The process employs cupric chloride in the presence of strong salt solutions, which are generally made up by dissolving copper sulfate in an aqueous solution of sodium chloride.



The cuprous chloride (CuCl) is soluble in the salt solution, and there is no precipitation. Under operating conditions, a certain amount of copper is retained by the sweetened liquid fuel, probably as cuprous mercaptides or cuprous chloride-olefin addition products, but these can be removed by washing the material with aqueous sodium sulfide. Air blowing the cuprous chloride solution, after or during the sweetening operation, regenerates the cupric chloride. The copper chloride solution may be employed as such, or the sour fraction may be percolated through a porous mass saturated with the treating agent. Alternatively, the liquid fuel may be mixed with a solid carrier for the reagent, dispersed as a slurry.

Three methods of mechanical application of the copper chloride are used. If air will not cause the fuel to change color or form gum, a fixed-bed process may be used in which the sour material is passed through beds of an adsorbent that have been impregnated with cupric chloride. Air continuously regenerates the cupric chloride almost simultaneously with the sweetening reaction.

In the solution process, a solution of cupric chloride is continuously mixed in a centrifugal pump with the sulfur-containing fuel. The mixture then enters a settling tank where the spent treatment solution separates from the liquid, and the treatment solution is withdrawn to a tank where blowing with air regenerates cupric chloride. The slurry process makes use of clay or a similar material impregnated with cupric chloride. The clay is mixed with a small amount of, say, naphtha to form a slurry, which is pumped into the sour naphtha stream. Air or oxygen gas is added with the sour stream and continuously regenerates the cupric chloride. The treated material and clay slurry flow into a settling tank and separate, and then the clay slurry is recycled.

Cord

A cord is a stack of wood comprising 128 ft^3 (3.62 m^3); standard dimensions are $4 \times 4 \times 8 \text{ ft}$, including air space and bark. One cord contains approximately 1.2 U.S. tons (oven-dry and equal to 2,400 lb). The name "cord" probably comes from the use of a cord or string to measure it.

Wood is an organic natural material, a composite of cellulose fibers embedded in a matrix of lignin. In the strict sense, wood is produced as secondary xylem in the stems of trees (and other woody plants) and has a support function, enabling woody plants to reach large sizes or to stand up for themselves. However, wood may also refer to other plant materials with comparable properties, and to material engineered from wood, or wood chips or fiber.

A cord of hard wood, such as ash or maple, is approximately equal in heating value to one ton of bituminous coal; soft woods, such as pine and poplar, have less than half this amount.

Firewood quantities are sometimes difficult to estimate. The official measurement of firewood is a "cord." To help you make an accurate estimate, here is how some common units of firewood measurement compare to the full cord.

Other terms, such as face cord, stove cord, or furnace cord, are sometimes used to describe a stack of wood measuring 4 ft. high, 8 ft. long with a piece length shorter than 4 ft. A common firewood piece length is 16 in., or one-third of a full cord, but other lengths are also available. Other non-legal definitions of firewood volume include

standing cord, kitchen cord, running cord, face cord, fencing cord, country cord, long cord, and rick. As none of these terms is a legally defined measurement, they are all subject to local variations. The only correct measurement of firewood and pulpwood is the cord and fractions thereof (e.g., half-cord, quarter-cord).

See also: Cellulose, Lignin, Wood.

Cordgrass

Spartina (*Spartina alterniflora*, cordgrass, cord-grass) contains 14 species, native to the coasts of the Atlantic Ocean in western and southern Europe, northwest and southern Africa, the Americas, and the southern Atlantic Ocean islands. One or two species also occur on the North American Pacific coast and in freshwater habitats inland in the Americas. The highest species diversity is on the east coasts of North America and South America, particularly Florida. They form large, often dense colonies, particularly on coastal salt marshes, and grow quickly and can vary in size from one to six feet tall.

Cordgrasses are perennial plants and spread by means of rhizomes to form clumps and mats which help to reduce erosion and reclaim land from the sea, and the root system of saltmarsh cordgrass helps stabilize the marsh mud. Taller than salt meadow cordgrass and with flat, smooth blades, saltmarsh cordgrass grows along the sides of guts (marsh creeks) and in places flooded by the tides. Cordgrasses are able to survive in areas flooded by salt water because of the regulatory system they have developed that excretes unneeded salt on the leaf edges.

Cordgrasses are expected to be able to produce good yields of biomass in poor soil conditions.

See also: Energy Crops, Miscanthus, Reed Canary Grass, Short Rotation Coppice.

Coriolis Force

The Coriolis force (sometimes called the Coriolis effect) is named after the French mathematician Gaspard-Gustave de Coriolis (1792–1843). The principle behind the Coriolis force is that because Earth rotates, any movement in the Northern Hemisphere is diverted to the right, if observed from a fixed position on the ground. In the Southern Hemisphere, the movement is to the left. This means that wind tends to rotate counterclockwise around low-pressure areas in the Northern Hemisphere and clockwise in the Southern Hemisphere.

The self-rotation of the Earth is an important factor to affect wind direction and speed. The Coriolis force, which is generated from the Earth's self-rotation, deflects the direction of atmospheric movements. In the north atmosphere, wind is deflected to the right and in the south atmosphere to the left. The Coriolis force depends on the latitude of the Earth – the force is zero at the equator and reaches maximum values at the poles. In addition, the amount of deflection on wind also depends on the wind speed; slowly blowing wind is deflected only a small amount, while stronger wind is deflected more.

In large-scale atmospheric movements, the combination of the pressure gradient due to the uneven solar radiation and the Coriolis force due to the self-rotation of the Earth causes the single meridional cell to break up into three convectional cells in each hemisphere: the Hadley cell, the Ferrel cell, and the Polar cell, and each cell has its own characteristic circulation pattern.

In the Northern Hemisphere, the Hadley cell circulation lies between the equator and north latitude 30°, dominating tropical and sub-tropical climates. The hot air rises at the equator and flows toward the North Pole in the upper atmosphere. This moving air is deflected by Coriolis force to create the northeast trade winds.

At approximately north latitude 30°, the Coriolis force becomes so strong to balance the pressure gradient force. As a result, the winds are deflected to the west. The air accumulated at the upper atmosphere forms the subtropical high-pressure belt and thus sinks back to the earth's surface, splitting into two components: one returns to the equator to close the loop of the Hadley cell; another moves along the surface of the Earth toward the North Pole to form the Ferrel Cell circulation, which lies between north latitude 30° and 60°. The air circulates toward the North Pole along the surface of the Earth until it collides with the cold air flowing from the North Pole at approximately north latitude 60°. Under the influence of the Coriolis force, the moving air in this zone is deflected to produce westerly winds. The Polar cell circulation lies between the North Pole and north latitude 60°. The cold air sinks down at the

North Pole and flows along the surface of the Earth toward the equator. Near north latitude 60° , the Coriolis effect becomes significant to force the airflow to southwest.

The Coriolis force does not explain wind direction in all places at all times. Local factors also determine the speed and direction of the wind. An example is a sea breeze. Land masses warm faster in the sun than water does. This means that the air over land expands and rises faster than the air over the sea. At night, the process is reversed, and wind tends to blow offshore, that is, from land out to sea. Mountain ranges also play tricks with the wind, diverting it in different directions. amounts of electricity for local use.

In summary, in the Northern Hemisphere, the Coriolis force turns the winds to the right. In the Southern Hemisphere, the Coriolis force turns the winds to the left. From 30° latitude to 60° latitude, the Ferrel Cell takes over and produces prevailing westerly winds at the surface within these latitudes.

See also: Atmosphere, Ferrel Cell, Hadley Cell, Polar Cell, Walker Circulation, Wind Energy, Wind Power.

Corn

Maize (corn) is a grass domesticated by indigenous peoples in Mesoamerica in prehistoric times. Native Americans cultivated it in numerous varieties throughout the Americas. After European contact with the Americas in the late 15th and early 16th centuries, explorers and traders carried maize back to Europe and introduced it to other countries through trade. Its use spread to the rest of the world.

Maize is the most widely grown crop in the Americas. Hybrid maize, because of its high-grain yield as a result of heterosis, is preferred by farmers over conventional varieties. While some maize varieties grow up to 23 feet tall, most commercially grown maize has been bred for a standardized height of approximately 8 feet). Sweet corn is usually shorter than field-corn varieties.

See also: Corn Stalks And Wheat Straw.

Corn Ethanol

Corn ethanol is ethanol produced from corn biomass and is the main source of ethanol fuel in many countries. It is debatable whether the production and use of corn ethanol results in lower greenhouse gas emissions than gasoline. There are two main types of corn ethanol production: (i) dry milling and (ii) wet milling which differ in the initial grain treatment method and co-products.

In the dry milling process, the entire corn kernel is ground into flour (often referred to as mash) which is then slurried by adding water. Enzymes are added to the mash to hydrolyze the starch into simple sugar derivatives. Ammonia is added to control the pH and as a nutrient for the yeast, which is added later. The mixture is processed at high temperatures to reduce the levels of the bacteria after which the mash is transferred and cooled in fermenters. Yeast is then added which causes the sugars to ferment into ethanol and carbon dioxide. The entire process takes approximately two days (40 to 50 hours), during which time the mash is kept cool and agitated to promote the activity of the yeast. The ethanol is purified through a combination of distillation and dehydration to create fuel ethanol. The mash is then transferred to distillation columns, where the ethanol is removed from the stillage. The ethanol is dehydrated to near-pure alcohol (200 proof alcohol) using a molecular sieve system. A denaturant such as gasoline is added to render the product undrinkable after which the product is then ready to ship to gasoline retailers or terminals. The remaining stillage is processed into a livestock feed (known as distiller's dried grains and solubles, DDGS). The carbon dioxide released from the process is used to carbonate beverages and for manufacturing cry ice (solid carbon dioxide).

In the wet milling process, the corn grain is separated into components by steeping it in dilute sulfuric acid for 24 to 48 hours. The slurry mix then passed through a series of grinders to separate out the corn germ. The remaining components of fiber, gluten and starch, and starch are segregated using screen, hydrocyclone, and centrifugal separators. The corn starch and remaining water can be fermented into ethanol through a similar process as dry milling, dried and sold as modified corn starch, or made into corn syrup. The gluten protein and steeping liquor are dried to

make a corn gluten meal that is sold to the livestock industry. The heavy steep water is also sold as a feed ingredient and used as an alternative to salt in the winter months. Corn oil is also extracted and sold.

See also: Corn Oil, Ethanol From Corn.

Corn Oil

Corn oil (maize oil) is oil extracted from the germ of corn (maize). The main use of corn oil is in cooking, where the high smoke point makes refined corn oil a valuable frying oil. Corn oil is also a feedstock used for biodiesel.

Typically, corn oil is expeller-pressed then solvent-extracted using a solvent such as hexane or 2-methyl pentane (isohexane) after which the solvent is evaporated from the corn oil, recovered, and re-used. After extraction, the corn oil is then refined by degumming and/or alkali treatment, both of which remove phosphatide derivatives. Alkali treatment also neutralizes free fatty acids and removes color (bleaching). The final steps in refining corn oil include the removal of wax derivatives, and deodorization by steam distillation of the oil at 232 to 260°C (450 to 500°F) under a high vacuum.

See also: Corn Ethanol.

Corn Stalks and Wheat Straw

From the agricultural sector, the major cellulosic resources are corn stalks and wheat straw. Both are left in the field after the grain is harvested in much of the U.S. While a portion of this residue does have a value in maintaining soil quality and crop productivity, in some higher yield areas of the United States, there is an excess of residue produced that could be beneficially removed. It is important to use this resource in a way that is environmentally and economically sound and that supplies the needs of biorefineries in terms of cost, quality, and consistency.

Corn stalks and wheat straws are the two agricultural residues produced in the largest quantities. However, many other residues such as potato and beet waste may be prevalent in some regions. In addition to quantity, it is necessary to consider density and water content (which may restrict the feasibility of transportation) and seasonality which may restrict the ability of the conversion plant to operate on a year-round basis. Facilities designed to use seasonal crops will need adequate storage space and should also be flexible enough to accommodate renewable feedstocks such as wood residues or other wastes in order to operate year-around. Some agricultural residues need to be left in the field in order to increase tilth (the state of aggregation of soil and its condition for supporting plant growth and to reduce erosion), but some residues such as corncobs can be removed and converted without much difficulty.

Similar to herbaceous crops, straw usually has lower moisture content than woody biomass. Conversely, it has a lower calorific value, bulk density, ash melting point and higher content of ash, and problematic inorganic component such as chlorine, potassium, and sulfur, which cause corrosion and pollution. The last two drawbacks can be relatively easily overcome by leaving straw on the field for a while. In such a way, rainfall “washes” it naturally from a large part of potassium and chlorine. Alternatively, fresh straw can be directly shipped to the gasification plant, where it is washed by dedicated facilities at moderate temperatures (50 to 60°C, 122 to 140°F). Due to washing, the initially low moisture content of straw becomes higher in both cases and hence a mandatory drying is applied afterwards. In both cases also, the content of corrosive components is reduced, but not completely taken out. In order to decrease handling costs, straw and dedicated herbaceous energy crops are usually baled before being shipped to the gasification plant. The weight and the size of bales depend on the baling equipment and on the requirements of the gasification plant.

Corn-to-Ethanol Process

Fermentation of sugars to ethanol (Figure 1), using commercially available fermentation technology, provides a fairly simple, straightforward means of producing ethanol with little technological risk. The system modeled assumes that

the molasses are clarified, and then fermented via cascade fermentation with yeast recycle. The stillage is concentrated by multiple-effect evaporation, and a molecular sieve is used to dehydrate the ethanol.

For more than 150 years in the United States, corn refiners have been perfecting the process of separating corn into its component parts to create a myriad of value-added corn products. The corn wet milling process separates corn into its four basic components, viz., starch, germ, fiber, and protein. There are several basic steps involved to accomplish this corn refining and alcohol fermentation process.

The corn wet milling process separates corn into its four basic components: starch, germ, fiber, and protein. The basic steps to accomplish this process are as follows. First, the incoming corn is inspected and cleaned. Then, it is steeped for 30 to 40 hours to begin breaking the starch and protein bonds. The next step in the process involves a coarse grind to separate the germ from the rest of the kernel. The remaining slurry consisting of fiber, starch, and protein is finely ground and screened to separate the fiber from the starch and protein. The starch is separated from the remaining slurry in hydrocyclones, after which the starch can be converted to syrup or it can be made into several other products through a fermentation process.

See also: Corn Ethanol, Wet Milling Process.

Corrosion

One aspect of energy production from any source is the potential of corrosion of the process equipment. Corrosion is a diffusion-controlled process that occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation, can increase a material's corrosion resistance.

In the corrosion process, a refined metal is converted to a more stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with the environment, but the mechanism of corrosion is not always predictable. The corrosion process degrades the useful properties of materials and structures including strength, appearance, and permeability to liquids and gases. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulfur. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxides or salts of the original metal, and may result in a distinctive coloration of the metal surface. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term degradation is more common.

See also: Corrosion by Fuel Ash.

Corrosion by Fuel Ash

One particular aspect of corrosion that deserves attention is the presence of alkali metals that occur in biomass and the presence of these metals in the ash after biomass combustion.

Fuel ash corrosion of components in process furnaces, utility boilers, and other equipment where fuels with a high metal content are fired is due to the effects of vanadium and sodium contained in the fuel. These metals are found in the form of organometallic complexes called porphyrins which are concentrated during the refining cycle in heavy residual fuels. In addition to these organometallic complexes, sources of additional metallic salts such as spent caustic and entrained salt in the crude are also concentrated in the heavy fuels. These salts act synergistically with the vanadium compounds present and can cause accelerated corrosion of metals and refractories in utility boiler and process furnaces when firing these types of fuels.

Sodium plus vanadium in the fuel in excess of 100 ppm can be expected to form fuel ashes corrosive to metals by fuel oil ashes.

See also: Corrosion.

p-Coumaryl Alcohol

See: Paracoumaryl Alcohol.

Counter-Current Fixed Bed Gasifier

The counter-current fixed bed gasifier (up draft gasifier) consists of a fixed bed of carbonaceous fuel (such as biomass) through which the gasification agent (steam, oxygen, and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag. The slagging gasifiers require a higher ratio of steam and oxygen to carbon in order to reach temperatures higher than the ash fusion temperature. The nature of the gasifier means that the fuel must have high mechanical strength and must be non-caking so that it will form a permeable bed, although recent developments have reduced these restrictions to some extent. The throughput for this type of gasifier is relatively low. Thermal efficiency is high as the gas exit temperatures are relatively low. However, this means that tar and methane production is significant at typical operation temperatures, so product gas must be extensively cleaned before use or recycled to the reactor.

The major advantages of this type of gasifier are its simplicity, high charcoal burn-out, and internal heat exchange leading to low gas exit temperatures and high gasification efficiency. In this way also, fuels with a high moisture content (up to 50% w/w) can be used. However, high amounts of tar and pyrolysis products are produced because the pyrolysis gas is not lead through the oxidation zone. This is of minor importance if the gas is used for direct heat applications, in which the tar is burned. In case the gas is used for engines, gas cleaning is required, resulting in problems of tar-containing condensates.

See also: Gasification, Gasifiers.

Covered Lagoon Digester

A digester is a sealed container or tank, where the biological digestion of organic waste (such as animal manure) can occur and biogas is formed.

A covered lagoon digester, as the name suggests, consists of a manure storage lagoon with a cover. The cover traps gas produced during decomposition of the manure. This type of digester is the least expensive of the three.

Typically covered lagoons are used with flush manure management systems that discharge manure at 0.5 to 2% solids. The in-ground, earth, or lined lagoon is covered with a flexible or floating gas tight cover. They are not heated and considered ambient temperature digesters. Retention time is usually 30-45 days or longer depending on lagoon size. In climates that have elevated year round temperatures, such as southern and western United States, these digesters can produce stable, reduced-odor, nutrient-rich effluent for application on fields and crops; pathogen and weed seed reduction and produce biogas for farm energy use. Heat recovery from the biogas can be used to heat nurseries on swine farms and warm milking parlors on dairy farms. Large lagoons in hot climates may produce sufficient quantity, quality, and consistency of gas to justify use in an engine generator. In areas with cooler climates, waste digestion, odor control, and gas production will be less consistent and the low-quality gas may need to be flared off much of the year for odor control and greenhouse gas reduction.

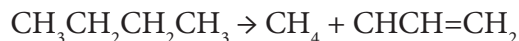
Covering a manure storage lagoon is a simple form of digester technology suitable for liquid manure with less than 3% solids. For this type of digester, an impermeable floating cover of industrial fabric covers all or part of the lagoon. A concrete footing along the edge of the lagoon holds the cover in place with an airtight seal. Methane produced in the lagoon collects under the cover. A suction pipe extracts the gas for use. Covered lagoon digesters require large lagoon volumes and a warm climate. Covered lagoons have low capital cost, but these systems are not suitable for locations in cooler climates or locations where a high water table exists.

See also: Digester.

Cracking

Cracking is a thermal process by which the constituents of a feedstock are converted to lower molecular weight products. The term cracking applies to the decomposition of carbonaceous constituents (such as biomass to produce bio-oil) that is induced by elevated temperatures ($>350^{\circ}\text{C}$, $>660^{\circ}\text{F}$) whereby the higher molecular weight constituents of crude oil are converted to lower molecular weight products. Cracking reactions involve carbon-carbon bond rupture and are thermodynamically favored at high temperature. Two general types of reaction occur during cracking that can be illustrated by simple equations:

The decomposition of large molecules into small molecules (primary reactions):



Reactions by which some of the primary products interact to form higher molecular weight materials (secondary reactions):



or



Thermal cracking is a free radical chain reaction; a free radical is an atom or group of atoms possessing an unpaired electron. Free radicals are very reactive, and it is their mode of reaction that actually determines the product distribution during thermal cracking. Free radical reacts with a hydrocarbon by abstracting a hydrogen atom to produce a stable end product and a new free radical. Free radical reactions are extremely complex, and it is hoped that these few reaction schemes illustrate potential reaction pathways. Any of the preceding reaction types are possible, but it is generally recognized that the prevailing conditions and those reaction sequences that are thermodynamically favored determine the product distribution.

In the cracking process, the aromatic ring is considered fairly stable at moderate cracking temperatures (350 to 500°C , 660 to 930°F). Alkylated aromatics, like the alkylated naphthenes, are more prone to dealkylation than to ring destruction. However, ring destruction of the benzene derivatives occurs above 500°C (930°F), but condensed aromatics may undergo ring destruction at somewhat lower temperatures (450°C , 840°F).

Catalytic cracking is the thermal decomposition of carbonaceous materials in the presence of a catalyst. Catalytic cracking also results in production of the maximum amount of butenes and butanes (C_4H_8 and C_4H_{10}) rather than ethylene and ethane (C_2H_4 and C_2H_6).

Clay minerals are a family of crystalline aluminosilicate solids, and the acid treatment develops acidic sites by removing aluminum from the structure. The acid sites also catalyze the formation of coke, and Houdry developed a moving bed process that continuously removed the cooked beads from the reactor for regeneration by oxidation with air. Although thermal cracking is a free radical (neutral) process, catalytic cracking is an ionic process involving carbonium ions, which are hydrocarbon ions having a positive charge on a carbon atom. The formation of carbonium ions during catalytic cracking can occur by either of the following processes: (i) addition of a proton from an acid catalyst to an olefin or (ii) abstraction of a hydride ion (H^-) from a hydrocarbon by the acid catalyst or by another carbonium ion.

However, carbonium ions are not formed by cleavage of a carbon-carbon bond. In essence, the use of a catalyst permits alternate routes for cracking reactions, usually by lowering the free energy of activation for the reaction. The acid catalysts first used in catalytic cracking were amorphous solids composed of approximately 87% silica (SiO_2) and 13% alumina (Al_2O_3) and were designated low-alumina catalysts. However, this type of catalyst is now being replaced by crystalline aluminosilicates (zeolites) or molecular sieves. The first catalysts used for

catalytic cracking were acid-treated clays, formed into beads. In fact, clays are still employed as catalyst in some cracking processes.

See also: Thermal Decomposition.

Cropland

Croplands are those lands dedicated to the growth of crops. The total cropland includes five components: cropland harvested, crop failure, cultivated summer fallow, cropland used only for pasture, and idle cropland.

Currently, the term croplands is often used more specifically to include those lands that are used to grow crops that can be converted into biofuel.

Cropland pasture is land used for long-term crop rotation. However, some cropland pasture is marginal for crop uses and may remain in pasture indefinitely. This category also includes land that was used for pasture before crops reached maturity and some land used for pasture that could have been cropped without additional improvement.

Crops

Biomass currently provides varying proportions (depending upon the country) of the primary energy supply. Projections are that this proportion will need to increase dramatically to meet growing energy demand. Given a relatively fixed land base, the production of energy crops will compete with traditional agricultural and forestry uses of land. It is essential that agriculture and forestry work together to create integrated biomass production systems that landowners can use to help meet the growing energy demands of the United States. Producing fast-growing short rotation woody crops on agricultural lands is one such approach that shows considerable promise. When produced in integrated systems, short rotation woody crops combine the goals of sustainable forestry with those of sustainable agriculture at multiple temporal and spatial scales. In addition to using woody biomass for energy for power and heat generation via co-firing and gasification, woody crops with their high hemicellulose and cellulose content are well suited for biorefining to yield liquid fuels such as ethanol, methanol, distillable oil (sometimes referred to as pyrolysis oil or bio-oil), and other products, such as biodegradable plastics and specialty chemicals.

Crops are the annual or seasonal yield of any plant that is grown to be harvested as food, as livestock fodder, fuel, or for any other economic purpose in significant quantities. This category includes crop species as well as agricultural techniques related to cropping. There are many types of crops that are used for industrial purposes. For example, crops are grown and harvested for the sole purpose of making profit and feeding people, as they are grown in large amounts in a certain area suitable for growing crops. Crops have essentially many functions and benefit particularly for the *human animal*! The products from crops are not only used as primary source of human foods and animal feed, but also as source of timber, fibers, and biomass energy. In addition, crops also have an essential function to maintain ecological systems and natural environment. Most of crop production is used as foods, but in the last century (the 20th century), crops were also cultivated for non-food use – examples are pharmaceutical and nutritional products, chemical derivative products such as adhesive, paints, polymer, plastics, and industrial oils in forms of bio diesel, transmission fluids, and lubricants.

Many efforts have been carried out to grow crops for foods production in order to strengthen food security, and to alleviate the hunger and poverty particularly in developing countries. However, serious consideration should also be directed toward cultivation of crops for non-food use.

Thus, by definition, energy crops are plants grown specifically for use as a fuel. Although growing crops for fuel date from medieval times, in their modern form, energy crops are the most recent and innovative renewable energy option. Energy crops are important as a renewable energy technology because their use will produce a variety of economic, environmental, and energy benefits (Lago et al., 2019). Commercial energy crops are typically densely planted, high-yielding crop species where the energy crops will be burnt to generate power. Woody crops such as willow and poplar are widely utilized, as well as tropical grasses such as miscanthus and elephant grass (*Pennisetum purpureum*).

Grasses are usually herbaceous plants with narrow leaves growing from the base. They include the true grasses of the Poaceae (or Gramineae) family, as well as the sedges (Cyperaceae) and the rushes (Juncaceae). The true grasses include cereals, bamboo, and the grasses of lawns (turf) and grassland. Sedges include many wild marsh and grassland plants, and some cultivated ones such as water chestnut (*Eleocharis dulcis*) and papyrus sedge (*Cyperus papyrus*). Most of the interest in grass biomass tends to focus on economics, but there is a list of traits that should be considered and valued when evaluating a potential solid biomass energy source. These traits are beneficial to society in general, or impact the suitability of biomass for a farm operation.

If the carbohydrate content is desired for the production of biogas, whole-crops, such as maize, Sudan grass, millet, white sweet clover, and many others, can be made into silage after which they can be converted into biogas. On the other hand, crop residues are the residues remaining after crops have been harvested. Crop residues typically contain 40% w/w of the nitrogen (N), 80% w/w of the potassium (K), and 10% w/w of the phosphorus (P) applied to the soil in the form of fertilizer. If these residues are subjected to direct combustion for energy, only a small percentage of the nutrients is left in the ash.

The valuable portion of sugar and starch crops (in terms of biofuel production) is the stalks and leaves, which are composed mainly of cellulose. The individual six-carbon sugar units in cellulose are linked together in extremely long chains by a stronger chemical bond than exists in starch. In *starch crops*, most of the six-carbon sugar units are linked together in long, branched chains (*starch*). Yeast cannot use these chains to produce ethanol. The starch chains must be broken down into individual six-carbon units or groups of two units. The starch conversion process is relatively simple because the bonds in the starch chain can be broken in an inexpensive manner by the use of heat and enzymes, or by a mild acid solution.

Sugar crops include a variety of plants such as fodder beets, fruit crops, Jerusalem artichokes, sugar beets, sugar cane, and sweet sorghum. Interest in ethanol production from such agricultural crops has prompted the development of sugar crops that have not been cultivated on a widespread commercial basis in many countries. Preparation is basically a crushing and extraction of the sugars which the yeast can immediately use. But sugar crops must be dealt with fairly quickly before their high sugar and water content causes spoilage. Because of the danger of such spoilage, the storage of sugar crops is not practical.

As with starch, cellulose must be broken down into sugar units before it can be used by yeast to make ethanol. However, the breaking of the cellulose bonds is much more complex and costly than the breaking of the starch bonds. Breaking the cellulose into individual sugar units is complicated by the presence of lignin, a complex compound surrounding cellulose, which is even more resistant than cellulose to enzymatic or acidic pretreatment (Hwang and Obst, 2003). Because of the high cost of converting liquefied cellulose into fermentable sugars, agricultural residues (as well as other crops having a high percentage of cellulose) are not yet a practical feedstock source for small ethanol plants.

Crop residues (cobs, stems, leaves, in particular straw, and other plant matter) left in agricultural fields after harvest could potentially be used for solid biofuels production. Due to high energy content, straw is one of the best crop residues for solid biofuels. However, straw has several disadvantages – it has a higher ash content, which results in lower calorific value. In order to improve its bulk density, the straw is generally baled before transportation. Straw burning requires a specific technology, and there are four basic types of straw burners: (i) the burners that accept shredded, loose straw, (ii) the burners that use densified straw products such as pellets, briquettes or cubes, and straw logs, (iii) the burners for small, square bale of feedstock, and (iv) the burners for round bales of feedstock. To be suitable for heat and electricity production, straw should not have a large content of moisture, preferably not more than 20% as the moisture reduces the boiler efficiency. Also, straw color as well as straw chemistry should be considered before burning as it indicates the quality of the straw. Most crop residues are returned to the soil, and the humus resulting from their decomposition helps maintain soil nutrients, soil porosity, water infiltration, and storage, as well as reducing soil erosion.

Wood is the oldest fuel known to man. Burning wood rather than fossil fuels can reduce the carbon dioxide emissions responsible for global climate change. Wood fuel is carbon dioxide (CO₂)-neutral. It gives off only as much carbon dioxide when burned as it stores during its lifetime. In addition, wood fuel has low levels of sulfur, a chemical that contributes to acid rain.

Regularly coppiced plantations will actually absorb more carbon dioxide than mature trees – since carbon dioxide absorption slows once a tree has grown. Growing crops for fuel, particularly wood coppice, offers very

promising developments for the future. Short rotation arable coppicing, using fast-growing willows, is currently seen as an important source of fuel for electricity generation. The overall process involves several stages – growing over two or three years, cutting and converting to wood chip, storage and drying, and transport to a power plant for combustion. And the combustion process can be very efficient, given the development of advanced co-generation techniques.

Moreover, the security of energy supply will be significantly enhanced for many crop-growing countries. Energy crop production and use could reduce dependency on imported oil, although complete energy independence will remain a possible future event.

See also: Crops-Residues, Energy Crops.

Crops – Residues

Crop residues and high yield-dedicated energy crops will not become cellulosic biomass supplies unless efficient, integrated biomass supply systems are developed. This means first of all, fully integrating crop production, harvesting and collection, storage, preprocessing, and transportation for each crop type and end use scenario.

Crop residues typically contain 40% of the nitrogen (N), 80% of the potassium (K), and 10% of the phosphorus (P) applied to the soil in the form of fertilizer. If these residues are subjected to direct combustion for energy, only a small percentage of the nutrients is left in the ash.

The valuable portion of sugar and starch crops (in terms of biofuel production) is the stalks and leaves, which are composed mainly of cellulose. The individual six-carbon sugar units in cellulose are linked together in extremely long chains by a stronger chemical bond than exists in starch. As with starch, cellulose must be broken down into sugar units before it can be used by yeast to make ethanol. However, the breaking of the cellulose bonds is much more complex and costly than the breaking of the starch bonds. Breaking the cellulose into individual sugar units is complicated by the presence of lignin, a complex compound surrounding cellulose, which is even more resistant than cellulose to enzymatic or acidic pretreatment. Because of the high cost of converting liquefied cellulose into fermentable sugars, agricultural residues (as well as other crops having a high percentage of cellulose) are not yet a practical feedstock source for small ethanol plants.

Crop residues (cobs, stems, leaves, in particular straw, and other plant matter) left in agricultural fields after harvest could potentially be used for solid biofuels production. Due to high energy content, straw is one of the best crop residues for solid biofuels. However, straw has several disadvantages – it has a higher ash content, which results in lower calorific value. In order to improve its bulk density, the straw is generally baled before transportation. Straw burning requires a specific technology. There are four basic types of straw burners: those that accept shredded, loose straw; burners that use densified straw products such as pellets, briquettes or cubes, and straw logs; small, square bale burners; and round bale burners. To be suitable for heat and electricity production, straw should not have a large content of moisture, preferably not more than 20% as the moisture reduces the boiler efficiency. Also, straw color as well as straw chemistry should be considered before burning as it indicates the quality of the straw.

Most crop residues are returned to the soil, and the humus resulting from their decomposition helps maintain soil nutrients, soil porosity, water infiltration, and storage, as well as reduce soil erosion.

See also: Cellulose, Crops, Starch, Straw

Cross Draft Gasifier

In a cross draft gasifier, the air enters from one side of gasifier reactor and gas is taken out from other side. The cross draft gasifier is one of the simplest gasifier designs. It has a quick start-up time (5 to 10 minutes) relative to the start-up time of the downdraft and updraft units and reaches high temperatures which may require air- or water-cooled nozzles.

Unlike downdraft and updraft gasifiers, the ash bin, fire, and reduction zone in cross draft gasifiers are separated. The design characteristics limit the type of fuel for operation to low ash fuels such as wood, charcoal, and coke. The

load following ability of cross draft gasifier is quite good due to concentrated partial zones which operate at temperatures up to 2,000°C (3,630°F). The relatively higher temperature in cross draft gas producer has an obvious effect on gas composition such as high carbon monoxide, and low hydrogen and methane content when dry fuel such as charcoal is used. Cross draft gasifier operates well on dry air blast and dry fuel.

The cross draft gasifier requires low tar fuels like charcoal and like most gasifiers, fuel size is important to avoid bridging. Cross draft gasifiers are not used all that often because other gasifier designs offer more flexibility and better performance across fuel types.

The advantages of the system lie in the small scale at which it can be operated.

In developing countries, installations for shaft power less than 10 kW are used due to the simple gas cleaning section (cyclone and baghouse filter). A drawback is the minimal tar cracking performance, resulting in the need for high-quality charcoal.

See also: Gasification.

Crude Oil

Crude oil (also called petroleum or oil) occurs in formations beneath the surface of the Earth and is commonly refined into various types of fuels. As a fossil fuel, crude oil is formed when large quantities of dead organisms, mostly zooplankton and algae, are buried underneath sedimentary rock and subjected to heat and pressure.

The components of crude oil are separated using fractional distillation which is the separation of the crude oil into fractions differing in boiling point by means of distillation using a fractionating column.

Crude oil consists of naturally occurring hydrocarbon derivatives of various molecular weights and may contain miscellaneous organic compounds containing nitrogen, sulfur, and oxygen as well as trace metals.

See also: Conventional Fuel Sources.

Cryogenic Dehydration

The traditional method of cooling is the Joule-Thomson (JT) valve where the gas is expanded through the JT valve where the pressure drop cools the gas, to 5 to 10°C below the minimum specified for the export pipeline, and into a cold separator where the gas stream liquids and water condense out and are removed. The dry gas is then cycled back through a heat exchanger to pre-cool the incoming gas and to be warmed itself. The main disadvantage of this process is that the gas loses pressure, and may require recompression.

A more energy-efficient process is to use a turbo expander. The gas expands through a turbine and thus cools itself before it goes into the cold separator. The turbine can be connected to a compressor which recompresses the gas with only a small loss in overall pressure, or, if pressure recovery is not required, the turbine can drive a generator to provide electric power. These processes can only be applied if the gas pressure after expansion is sufficiently high for condensation of the heavier components to take place. If the gas arrives at low pressure, however, say less than 50 bar, an external mechanical refrigeration plant must be used to cool it to the specified temperature.

Flowing the gas through a bed of silica gel would remove hydrocarbons and water by adsorption. The bed can then be regenerated by passing hot dry gas over it. A bed of alumina would operate as a molecular sieve to remove only the water. These latter processes are easy to start up and to operate at high 'turn down' (changes in throughput), and so are useful for variable and 'on-off' operation.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Cryogenic Equipment

This category of equipment contains turbo-expanders and the equipment associated with them. This category of equipment was not identified in the GRI study and so is a 'new' source of methane emissions. The total emissions

from turbo-expanders are small and contribute less than 3% of total methane emissions in a gas plant. The individual components contributing to emissions are valves, connectors, pressure-relief valves, compressor seals, and open-ended lines.

Cryogenic Expander Process

In the cryogenic expander process, a turboexpander is used to produce the necessary refrigeration and low temperatures, and high recovery of low-boiling components, such as ethane and propane, can be attained. Essentially, cryogenic processing consists of lowering the temperature of the gas stream to approximately -85°C (-120°F). There are several ways to perform this function, but the turbo expander process (in which external refrigerants are used to chill the gas stream) is the most effective. The quick drop in temperature that the expander is capable of producing condenses the hydrocarbons in the gas stream, but maintains methane in its gaseous form.

In the process, the gas stream is first dehydrated using a molecular sieve followed by cooling. The separated liquid containing most of the heavy fractions is then demethanized, and the cold gases are expanded through a turbine that produces the desired cooling for the process. The expander outlet is a two-phase stream that is fed to the top of the demethanizer column. This serves as a separator in which: (i) the liquid is used as the column reflux and the separator vapors combined with vapors stripped in the demethanizer are exchanged with the feed gas, and (ii) the heated gas, which is partially recompressed by the expander compressor, is further recompressed to the desired distribution pressure in a separate compressor. This process allows for the recovery of approximately 90 to 95% v/v of the ethane originally in the gas stream. In addition, the expansion turbine is able to convert some of the energy released when the gas stream is expanded into recompressing the gaseous methane effluent, thus saving energy costs associated with extracting ethane.

The cryogenic method is better at extraction of the lower-boiling liquids, such as ethane, than is the alternative absorption method.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Cryogenic Separation

Cryogenic separation units operate by cooling the gas and condensing some, or all, of the constituents for the gas stream. Depending on the product purity required, separation may involve flashing or distillation. Cryogenic units offer the advantage of being able to separate a variety of products from a single feed stream. One specific example is the separation of low-boiling olefins from a hydrogen stream. Hydrogen recovery is in the range of 95%, with purity above 98% obtainable.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Cryosphere

The cryosphere is the collective term for the components of the Earth system that contain a substantial fraction of water in the frozen state (Table C-10). The cryosphere comprises several components: snow, river, and lake ice; sea ice; ice sheets, ice shelves, glaciers and ice caps; and frozen ground which exist, both on land and beneath the oceans, and the lifespan of each component is different. For example, river ice and lake ice are transient features that generally do not survive from winter to summer while sea ice advances and retreats with the seasons, and in Arctic region, the sea ice can survive to become multi-year ice lasting several years. Nevertheless, all components of the cryosphere are inherently sensitive to changes in air temperature and precipitation, and hence to a changing climate.

Table C-10 The main components of the Earth system.

System	Description
Atmosphere	The gaseous layer surrounding the earth and held to its surface by gravity; receives energy from solar radiation which warms the surface of the Earth and is re-emitted and conducted to the atmosphere; also absorbs water from the surface of the Earth via the process of evaporation and then acts to redistribute heat and moisture across the surface of the Earth. In addition, the atmosphere contains substances that are essential for life, including carbon, nitrogen, oxygen, and hydrogen.
Aquasphere	This consists of those parts of the earth system composed of water in its liquid, gaseous (vapor), and solid (ice) phases; includes: the oceans and seas, ice sheets, sea ice, glaciers, lakes, rivers, streams, atmospheric moisture, ice crystals, and areas of permafrost. The aquasphere includes both saltwater and freshwater systems as well as the moisture found in the soil (soil water) and within rocks (groundwater). In some classifications, the aquasphere is sub-divided into the fluid water systems (the hydrosphere) and the ice systems (the cryosphere).
Geosphere	The part of the Earth that is composed of rock and minerals; includes the solid crust, the molten mantle and the liquid and solid parts of the core of the Earth. In many places, the geosphere develops a layer of soil in which nutrients become available to living organisms, and which thus provides an important ecological habitat and the basis of many forms of life. The surface of the geosphere is subject to processes of erosion, weathering and transport, as well as to tectonic forces and volcanic activity, which result in the formation of landforms such as mountains, hills and plateaus.

Crystallization

Crystallization is the process of generating a solid crystalline material from a vapor, a melt, or a solution. In the first two cases, the crystallization is caused by cooling the medium to below the melting point of the crystals, after which the crystals separate from the vapor or the melt as solid crystals rather than as liquids and can be removed by settling, filtration, centrifuging, or cycloning.

When crystallizing from a saturated solution, the amount of solids that can remain dissolved in the liquid is reduced either by cooling – which is used where the solubility of the solids is a strong function of temperature – or by removal of liquid by evaporation – which is used when solubility is relatively insensitive to temperature.

The major advantage of crystallization over other separation methods is the ability of the process to precipitate essentially pure solids from a solution in a single stage. However, the process does not completely remove all of the solid material from the solution and further treatment of the residual saturated mother liquor is usually required.

The three requirements for solids crystallization from a solution are (i) the achievement of supersaturation, (ii) the nucleation of crystals, and (iii) crystal growth.

See also: Evaporation.

CTSL Process

The CTSL process (catalytic two-stage liquefaction process) was originally developed for the production of liquids from coal and is a further development of the H-Coal single-stage process and has been advocated as a means of producing biofuel from biomass.

In the process, the feedstock is slurried with a process-derived recycle solvent, preheated, mixed with hydrogen, and fed to the bottom of an ebullating bed reactor. This reactor contains a supported catalyst, generally nickel-molybdenum on alumina, which is fluidized by an internal recycle in the reactor. The reactor, therefore, has the characteristics of a uniform-temperature continuous-stirred tank reactor. The solvent acts as a hydrogen donor and solubilizes the coal by breaking down its structure to a substantial extent in the first reactor. This first reactor substantially dehydrogenates the solvent. Typically, operating conditions are on the order of 2,500 psi and a temperature of 400 to 410°C (750 to 770°F) but with biomass, the temperature may vary with the characteristics of the biomass feedstock.

The reactor products pass directly into the base of a second, ebullating-bed reactor stage, operating at the same pressure as the first stage but at a higher temperature (approximately 430 to 440°C, 805 to 825°F). This reactor also contains a supported catalyst, generally but not necessarily the same as that in the first reactor.

After separation and depressurization steps, the products from the second reactor enter an atmospheric distillation column, where distillate products boiling up to 400°C (750°F) are removed. The bottom stream from this column contains solvent, carbonaceous material, unreacted coal, and mineral matter. These solids are removed by one of several possible techniques and the solvent is recycled to the slurrying step. In some process variants, only part of the atmospheric column bottom stream is routed to the solids removal step, resulting in the recycle solvent containing mineral matter and any dispersed catalyst that may have been used.

See also: Liquefaction.

Cull Tree

A cull tree is a live tree, 5.0 in diameter at breast height (dbh) or larger that is cannot be used for sawing logs now or prospectively because of rot, roughness, or species.

A rough cull tree is a tree that does not meet regional standards that are required for sale because of excessive sound cull. This definition may also include noncommercial tree species.

A rotten cull tree is a tree that does not meet regional standards that are required for sale because of excessive unsound cull. This definition may also include noncommercial tree species.

See also: Wood.

Cultivated Summer Fallow

Summer fallow is land uncropped and plowed during the summer, in order to pulverize the soil and kill the weeds. It is also cropland in semi-arid regions that is purposely kept out of production during a cropping season mainly to conserve moisture for the next season. It is common for wheat producers in semi-arid regions to rotate half their cropland to summer fallow each year.

Cultivated summer fallow refers to cropland in sub-humid regions of the Western United States cultivated for a season or more to control weeds and accumulate moisture before small grains are planted. This practice is optional in some areas but necessary in the drier cropland areas of the West. Other types of fallow, such as cropland planted to soil improvement crops but not harvested, and cropland left idle all year, are not included in cultivated summer fallow.

See also: Crops, Crops-Residues.

Current Reserves

Current reserves are those resources that can profitably be extracted at current prices. Even though current reserve is usually given as a number, it usually fluctuates with prices. Sometimes, the current reserves are listed as the recoverable reserves (Table C-11).

Table C-11 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Potential reserves represent the relationship between the market price for the resource and the amount of the resource that can be profitably extracted at that price. The higher the price, the greater the potential reserves.

See also: Reserves.

Cyclone Separation

A cyclone separator is a device for removing particulate matter from air or other gas streams and is a mechanically-aided collector that uses inertia to separate particulate matter from the gas stream as it spirals through the cyclone. Cyclone separators are generally used for collection of medium-sized and coarse particles.

Cyclones have a relatively simple construction and generally have no moving parts. Simple cyclones consist of (i) an inlet cylindrical section, (ii) a conical section, (iii) an outlet gas duct, (iv) an outlet dust tube, and (v) a collection hopper. A cyclone uses an induced draft fan to move the gas stream through the device. They are sized to provide the maximum inlet velocity possible for high separation without excessive turbulence. Multiple-cyclone separators consist of a number of small-diameter cyclones, operating in parallel and having a common gas inlet and outlet. Multiclones operate on the same principle as cyclones—creating a main downward vortex and an ascending inner vortex.

In general, a cyclone consists of an upper cylindrical part referred to as the barrel and a lower conical part referred to as cone. The air stream enters tangentially at the top of the barrel and travels downward into the cone forming an outer vortex. The increasing air velocity in the outer vortex results in a centrifugal force on the particles. Because of inertia, the particles resist the direction change as the gas turns, and they migrate toward the cylinder walls, separating them from the air stream. When the air reaches the bottom of the cone, an inner vortex is created reversing direction and exiting out the top as clean air while the particulates fall into the dust collection chamber attached to the bottom of the cyclone. The collection efficiency of a cyclone separator improves as the number of revolutions made by the gas and the gas velocity increase. However, the overall performance depends on the particle size distribution of the incoming gas stream.

A cyclone separator uses the centrifugal force created by a spinning gas stream to separate particles from a gas. The particulate-laden gas enters tangentially near the top of the device. The shape of the cyclone and the tangential entry force the gas flow into a downward spiral. Centrifugal force and inertia cause the particles to move outward, collide with the outer wall, and then slide downward to the bottom of the device. Near the bottom of the cyclone, the gas reverses its downward spiral and moves upward in a smaller inner spiral. The clean gas exits from the top through a vortex-finder tube, and the panicles exit from the bottom of the cyclone through a pipe sealed by a spring-loaded flapper valve or a rotary valve.

A cyclone separator can be constructed of any material, metal or ceramic that is capable of withstanding high temperatures, abrasive particles, or corrosive atmospheres. It is necessary that the interior surface of the separator is smooth so that the collected particles may slide easily down the wall to the hopper. The most common types of centrifugal, or inertial, collectors currently in use are single-cyclone separators and multiple-cyclone separators (multiclone).

See also: Centrifugal Separation, Gas Cleaning, Gas Processing, Gas Treating Particulate Matter Removal.

Cycloparaffin Hydrocarbons

Cycloparaffin hydrocarbons (also referred to as naphthenes) are hydrocarbon derivatives that contain a saturated ring system. These include derivatives of cyclopentane, cyclohexane, and decahydronaphthalene (decalin). In theory, the ring system may be built up of a varying number of carbon atoms, and among the synthesized hydrocarbons, there are individual constituents with rings of the three-, four-, five-, six-, seven-, and eight-carbon atoms (Table C-12). Thermodynamic studies show that naphthene rings with five and six carbon atoms are the most stable. The naphthenic acids contain chiefly cycle pentane as well as cyclohexane rings.

Table C-12 Types of cycloalkanes.

Alkane	Formula	Boiling point, °C	Melting point, °C	Liquid density*
Cyclopropane	C ₃ H ₆	−33	−128	
Cyclobutane	C ₄ H ₈	12.5	−91	0.720
Cyclopentane	C ₅ H ₁₀	49.2	−93.9	0.751
Cyclohexane	C ₆ H ₁₂	80.7	6.5	0.778
Cycloheptane	C ₇ H ₁₄	118.4	−12	0.811
Cyclooctane	C ₈ H ₁₆	149	14.6	0.834
Cyclononane	C ₉ H ₁₈	69	10-11	0.8534
Cyclododecane	C ₁₀ H ₂₀	201	9-10	0.871

Density of the liquid, g·cm^{−3} (at 20°C).

Cycloalkanes are similar to alkanes in terms of the general physical properties, but a cycloalkane has a higher boiling point, a higher melting point, and a higher density than the corresponding n-alkane.

The principal structural variation of cycloalkane derivatives is the number of rings present in the molecule. The mono- and bicyclic naphthene derivatives are generally the major types of cycloparaffins that occur in nature, with the boiling point or molecular weight increased by the presence of alkyl chains.

See also: Naphthenes.

Darcy's Law

For laminar single fluid flows in straight ducts, the flow resistance or pressure drop is proportional to the flow rate. The same relationship holds for flow in curved ducts when the flow velocity is small. This unique relationship between the flow velocity and the pressure drop can be generalized to the flow through porous media:

$$\frac{dp}{dx} - \rho g_x \propto -u$$

In this equation, u is the superficial fluid flow velocity (or discharge rate per unit cross-sectional area), p is the fluid pressure, x is the linear coordinate in the flow direction, ρ is the fluid density, and g_x is the gravity in the direction of flow. This limiting flow behavior has received great attention for centuries. It has been the basis for macroscopic modeling flow through packed beds; the proportionality constant can be determined if a flow geometry is defined.

A one-dimensional empirical model continuum, for saturated single fluid flow in porous media, was based on the proportionality, and Darcy's law can also be expressed as:

$$u = -\frac{k}{\mu} \left(\frac{\partial p}{\partial x} - \rho g_x \right)$$

In this equation, k is the permeability of the porous medium which is assumed to be constant in applications and μ is the dynamic viscosity of the fluid. Darcy's law has been generalized to be used for multi-dimensional single-phase and multiphase flows. Here, multiphase flows specifically mean immiscible multiphase flows. For miscible systems, one can effectively treat them as single-phase flows.

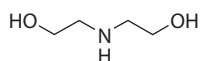
For single-phase flows, Darcy's law lacks both the flow diffusion effects and the inertial effects. Therefore, the utility of Darcy's law is restrictive and validation of the modeling results is often necessary. Remedies of these defects have been adjusted by addition of a diffusion term to the Darcy's law:

$$\nabla p - \rho \mathbf{g} = -\frac{\mu}{k} \mathbf{v} + \tilde{\mu} \nabla^2 \mathbf{v}$$

$\tilde{\mu}$ is an effective viscosity and $\mathbf{v}$ is the superficial fluid flow velocity. In general, the effective viscosity $\tilde{\mu}$ is proportional to the fluid viscosity μ and is affected by the type of porous media. For simplicity and convenience, the effective viscosity is usually taken to be identical to the fluid viscosity.

DEA

Diethanolamine, often abbreviated as DEA, is an organic compound with the formula $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$:



Diethanolamine

This colorless liquid is polyfunctional, being a secondary amine and a di-alcohol. Like other organic amines, diethanolamine acts as a weak base. DEA is soluble in water, even hygroscopic.

The alkanolamine derivatives and their aqueous solutions will absorb carbon dioxide and hydrogen sulfide at lower temperatures and release the acid gases at higher temperatures. This forms the basis for processes which separate carbon dioxide and hydrogen sulfide from gas streams.

Methyldiethanolamine is an alkanolamine used in gas treating and hydrogen sulfide enrichment units for selectively removing hydrogen sulfide from gas streams containing carbon dioxide. These units will, in most cases, permit 60 to 80% of the carbon dioxide to remain in the treated gas stream. Methyldiethanolamine is also used in natural gas plants for the bulk removal of carbon dioxide while producing a gas stream containing 0.25 grains hydrogen sulfide/100 ft³. Bulk carbon dioxide removal can be realized with methyldiethanolamine when the CO₂/H₂S ratio ranges from 100 to 1,000.

Similar compounds are monoethanolamine (MEA, H OCH₂CH₂NH₂), a primary amine, and diethanolamine (DEA, HOCH₂CH₂NHCH₂CH₂OH), a secondary amine, both of which are also used for in amine (olamine) gas treating units (Figure 4).

See also: Gas Cleaning, Gas Processing, Gas Treating.

Dehydration

Dehydration is the removal of water removal from gas streams, and there are several methods of dehydrating natural gas. The most common of these are liquid desiccant (glycol) dehydration, solid desiccant dehydration, and refrigeration (i.e., cooling the gas). However, the choice of dehydration method is usually between glycol and solid desiccants. Several other dehydration technologies (i.e., membranes, vortex tube, and supersonic processes) are less commonly used.

The first step in evaluating and/or designing a gas dehydration system is to determine the water content of the gas as a means of estimating water production with sour gas in the plant inlet separator. There are several methods available for determining the water content of sour gas streams at saturation, and one method is chart-based and provides good estimates of the equilibrium water vapor content of sour natural gas for a range of conditions including: hydrogen sulfide contents of 3 to 38 mole % with carbon dioxide contents of 3 to 43 mole %, pressures from 290 to 10,153 psi, and temperatures from 10 to 175°C (50 to 347°F). However, the error of this method can be as much as ±10%.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Dehydration – Glycol Process

Among the different gas drying processes, absorption is the most common technique, where the water vapor in the gas stream becomes absorbed in a liquid solvent stream. Glycol derivatives are the most widely used absorption liquids as they approximate the properties that meet commercial application criteria. Several glycols have been found suitable for commercial application (Table D-1).

Table D-1 Examples of glycol derivatives used for dehydration of gas streams.

Glycol derivative	Description
Monoethylene glycol (MEG)	Has a high vapor equilibrium with gas. Tends to lose to gas phase in contactor. Suitable for use as hydrate inhibitor where it can be recovered from gas by separation at temperatures below 10°C (50°F).
Diethylene glycol (DEG)	Has a high vapor pressure that leads to high losses in the contactor. Low decomposition temperature requires low re-concentrator temperature (157 to 171°C; 315 to 340°F) and thus cannot get pure enough for most applications.
Triethylene glycol (TEG)	The most common glycol used. Reconcentrated at 171 to 204°C (340 to 400°F) for high purity. At contactor temperatures in excess of 49°C (120°F), there is a tendency to high vapor losses.
Tetraethylene glycol (TREG)	Less loss at high gas contact temperatures than TEG. Reconcentrated at 204 to 221°C (400 to 430°F).

Triethylene glycol is by far the most common liquid desiccant used in natural gas dehydration. It is regenerated more easily to a concentration of 98 to 99% in an atmospheric stripper because of its high boiling point and decomposition temperature. It also has an initial theoretical decomposition temperature of approximately 205°C (405°F), whereas that of diethylene glycol is approximately 165°C (328°F). Vaporization losses with triethylene glycol are lower than with monoethylene glycol or with diethylene glycol. Therefore, triethylene glycol can be regenerated easily to the high concentrations needed to meet pipeline water dew point specifications.

In the process, wet natural gas first typically enters an inlet separator to remove all liquid hydrocarbon derivatives from the gas stream. Then, the gas flows to an absorber (contactor) where it is contacted countercurrently and dried (water is removed) by the lean triethylene glycol.

Triethylene also absorbs volatile organic compounds (VOCs) that vaporize with the water in the reboiler. Dry natural gas exiting the absorber passes through a gas/glycol heat exchanger and then into the sales line. The wet or rich glycol exiting the absorber flows through a coil in the accumulator where it is preheated by hot lean glycol. After the glycol-glycol heat exchanger, the rich glycol enters the stripping column and flows down the packed bed section into the reboiler. Steam generated in the reboiler strips absorbs water and volatile organic compounds out of the glycol as it rises up the packed bed. The water vapor and desorbed natural gas are vented from the top of the stripper. The hot regenerated lean glycol flows out of the reboiler into the accumulator (surge tank) where it is cooled via cross exchange with returning rich glycol; it is pumped to a glycol/gas heat exchanger and back to the top of the absorber.

The process efficiency can be improved by additional equipment such as a cooling coil for the rich glycol stream that controls the water reflux rate at the top of the stripper and which ensures that the water vapor leaving the still does not carry over excess glycol. In addition, heat exchange between the cool rich glycol and the hot lean glycol is improved by using two or more shell and tube heat exchangers in series. The increased heat recovery reduces fuel consumption in the reboiler and protects the glycol circulation pump from being overheated; it also allows the flash tank and filter to operate at approximately 65°C (150°F). Higher flash temperatures will ensure maximum entrained gas to be removed from the rich triethylene glycol.

Dehydration – Solid Desiccant

Solid desiccant dehydration systems work on the principle of adsorption. Adsorption involves a form of adhesion between the surface of the solid desiccant and the water vapor in the gas. The water forms an extremely thin film that is held to the desiccant surface by forces of attraction, but there is no chemical reaction.

Solid desiccant dehydrators are typically more effective than glycol dehydrators, as they can dry a gas to less than 0.1 ppm v/v (0.05 lb/MMscf). However, in order to reduce the size of the solid desiccant dehydrator, a glycol dehydration unit is often used for bulk water removal. The glycol unit would reduce the water content to around 60 ppm v/v, which would help reduce the mass of solid desiccant necessary for final drying.

Using desiccant dehydrators as alternatives to glycol dehydrators can yield significant economic and environmental benefits, including reduced capital cost, reduced operation and maintenance cost, and minimal volatile organic compounds and hazardous air pollutants (BTEX – benzene, toluene, ethylbenzene, and xylenes).

The capacity of a desiccant for water is expressed normally in mass of water adsorbed per mass of desiccant. The dynamic moisture sorption capacity of a desiccant will depend on a number of factors, such as the relative humidity of the inlet gas, the gas flow rate, the temperature of the adsorption zone, the mesh size of the granule, and the length of service and degree of contamination of the desiccant and not the least on the desiccant itself. The moisture sorption capacity is not affected by variations in pressure, except where pressure may affect the other variables listed previously. There are three capacity terms used: (i) static equilibrium capacity, which is the water capacity of new, virgin desiccant as determined in an equilibrium cell with no fluid flow – corresponding to the adsorption isotherm, (ii) dynamic equilibrium capacity, which is the water capacity of desiccant where the fluid is flowing through the desiccant at a commercial rate, and (iii) the useful capacity, which is the design capacity that recognizes loss of desiccant capacity with time as determined by experience and economic consideration and the fact that all of the desiccant bed can never be fully utilized.

A variety of solid desiccants are available in the market for specific applications. Some are good only for dehydrating the gas, whereas others are capable of performing both dehydration and removal of heavy hydrocarbon components. The selection of proper desiccant for a given application is a complex problem. For solid desiccants

used in gas dehydration, the following properties are desirable: (i) a high adsorption capacity at equilibrium which lowers the required adsorbent volume, allowing for the use of smaller vessels with reduced capital expenditures and reduced heat input for regeneration, (ii) a high selectivity, which minimizes the undesirable removal of valuable components and reduces overall operating expenses, (iii) easy regeneration since the relatively low regeneration temperature minimizes overall energy requirements, (iv) low pressure drop, (v) good mechanical properties – such as high crush strength, low attrition, low dust formation, and high stability against aging – which lower the overall maintenance requirements by reducing the frequency of adsorbent change out and minimizing downtime-related losses in production, and (vi) materials that are noncorrosive, nontoxic, chemically inert, high bulk density and no significant volume changes upon adsorption and desorption of water.

The most common commercial desiccants used in dry bed dehydrators are silica gel, molecular sieves, and activated alumina. Silica gel (a generic name for a gel manufactured from sulfuric acid and sodium silicate) is a widely used desiccant, which can be used for gas and liquid dehydration and hydrocarbon recovery from natural gas. It is characterized by the following: (i) best suited for normal dehydration of natural gas, (ii) easily regenerated compared to molecular sieves, (iii) has high water capacity, where it can adsorb up to 45% of its own weight in water, (iv) capable of dew points to 60°C (140°F), and (v) costs less than molecular sieve. Silica gel used for natural gas drying should be water-stable – many types of silica gel will produce fines in contact with water.

Molecular sieves are crystalline alkali metal aluminosilicates comprising a three-dimensional interconnecting network of silica and alumina tetrahedral. The structure is an array of cavities connected by uniform pores with diameters ranging from approximately 3 to 10 Å, depending on the sieve type. A molecular sieve is the most versatile adsorbent because it can be manufactured for a specific pore size, depending on the application. It is (i) capable of dehydration to less than 0.1 ppm water content, (ii) the overwhelming choice for dehydration prior to cryogenic processes, which is especially true for liquefied gas, (iii) excellent for removal of hydrogen sulfide and carbon dioxide, as well as dehydration, high temperature dehydration, high-boiling hydrocarbon liquids, and highly selective removal, (iv) more expensive than silica gel, but offers greater dehydration, and (v) requires higher temperatures for regeneration, thus has a higher operating cost.

A molecular sieve dehydration system is also an alternative to the Drizo process. However, because of multiple high pressure and high temperature vessels, the installed cost of a molecular sieve system is two or three times more than an equivalent Drizo system.

There are several types of alumina available for use as a solid desiccant. Activated alumina is a manufactured or natural occurring form of aluminum oxide that is activated by heating. It is widely used for gas and liquid dehydration and will produce a dew point below -158°F if applied properly. Less heat is required to regenerate alumina than for molecular sieve, and the regeneration temperature is lower. However, molecular sieves give lower outlet water dew points.

It should be noted that no desiccant is perfect or best for all applications. In some applications, the desiccant choice is determined primarily by economics. Sometimes, the process conditions control the desiccant choice. If a unit is designed properly, it is quite rare that desiccants can be interchangeable. What is often possible is to replace within one class of adsorbents, i.e., molecular sieve of one supplier with molecular sieve from another.

During the adsorption step, the gas to be processed is sent on the adsorbent bed, which selectively retains the water. When the bed is saturated, hot gas is sent to regenerate the adsorbent. After regeneration and before the adsorption step, the bed must be cooled. This is achieved by passing through cold gas. After heating, the same gas can be used for regeneration. In these conditions, four beds are needed in practice in cyclic operation to dry the gas on a continuous basis: two beds operating simultaneously in adsorption or gas drying cycle, one bed in the cooling cycle, and one bed in the regeneration cycle.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Dehydrator Systems

Many gas dehydrator systems use triethylene glycol (TEG) to remove water from the natural gas stream in order to meet pipeline specifications. Often, the glycol circulation rate is set much higher than it needs to be in order to achieve this objective. Over-circulation leads to increased methane emissions. Operators can adjust this circulation rate at no additional cost and decrease methane emissions from the dehydrator system. Another way to decrease

methane emissions from triethylene glycol systems is to install flash tank separators. Flash tank separators capture approximately 90% of the methane entrained in the triethylene glycol systems, preventing the methane from being boiled off into the atmosphere when the triethylene glycol systems passes through the regenerator.

Desiccant dehydrators can be good alternatives to triethylene glycol systems under certain circumstances. Glycol dehydrators can be replaced altogether with desiccant dehydrators at a higher cost, nearly eliminating gas emissions and also saving both fuel gas used for the glycol reboiler (sometimes a gas heater) and pneumatic gas used for glycol-unit controllers. With no regenerator, desiccant dehydrators produce methane emissions only when they are being refilled with desiccant, and even then the volumes are far below those from triethylene glycol systems.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Delignification

The alkaline delignification of wood in the pulp industry is an example of a particularly complex system involving hundreds of reactions. This process is the key step in the production of cellulose via chemical pulping. The lignin material in the wood is partially decomposed and dissolved in the treating liquor, whereas cellulose fibers remain in a solid state; part of the hemicellulose constituents is also dissolved.

The chemical complexity and large variations in wood composition plays a major role in the efficiency of the process. The key concept is to identify the most important reactions and to merge certain classes of compounds, much in line with an understanding of crude oil refining and petrochemical. The apparatus used in the paper and pulp industry is somewhat different from that used in the crude oil industry or classical chemical industry.

The removal of lignin from the wood has traditionally taken place by the Kraft process. This usually involves digesting wood chips at high temperature and pressure, and in a solution of sodium hydroxide and sodium sulfide in water (white liquor). The white liquor chemically dissolves the lignin bonds that interconnect the cellulose fibers.

At this stage, the solid pulp is brown (brown stock) and the combined liquids (known as black liquor) contain the lignin fragments along with chemicals and by-products. The pulp is separated from the used cooking liquors by a series of washes. The lignin fragments are collected and burned to help power the factory. The rest of the process is designed to recycle the heat and cooking chemicals.

Some by-products of the Kraft process are turpentine and tall oil, which is a viscous material with a variety of industrial uses. The brown stock produced by the Kraft process contains approximately 5% w/w of residual lignin, and is further delignified by a series of bleaching stages. Bleaching removes additional lignin, making the paper brighter.

Oxygen delignification is a process that removes more lignin, and uses fewer chemicals. It involves treating the pulp with oxygen in a pressurized vessel at a high temperature in alkaline solution, which is followed by a washing stage. The amount of residual lignin can be decreased to approximately 1.5% with this method, thus limiting the degree of bleaching needed to make paper from the pulp.

The delignification process has traditionally focused on wood pulp for paper and fiberboard, but more recent efforts involved the use of biomass as a source of ethanol – an alternative to fossil fuels. This plant material must undergo delignification before it can be used for this purpose. Microbial systems are being engineered that combine the removal of lignin with the conversion of cellulose to ethanol.

See also: Lignin.

Densification

Densification, such as briquetting or pelletization, is an important technique to densify biomass materials for increasing the particle size and bulk density. The reasons for biomass include (i) densified biomass is less expensive to transport, (ii) densified products are easier to store and handle, and (iii) densification enables certain biomass feedstocks to be gasified in a specific gasifier.

In its natural form, most biomass is difficult to utilize as a fuel because it is bulky, wet, and dispersed. Disadvantages of biomass as an energy source include inefficient transportation and large volumes required for storage. Solving these problems is where biomass densification gains extreme importance. Biomass densification is defined as compression

or compaction of biomass to remove inter- and intra-particle voids. Compression baling can reduce biomass volume to one-fifth of its loose bulk volume.

Densification of biomass is often necessary to combat the negative storage and handling characteristics of these low bulk density materials. A consistent, high-quality densified product is strongly desired, but not always delivered. Within the context of pelletizing and briquetting, binding agents are commonly added to comminuted biomass feedstocks to improve the quality of the resulting pellets or briquettes. Many feedstocks naturally possess such binding agents; however, they may not be abundant enough or available in a form or state to significantly contribute to product binding. Also, process parameters (pressure and temperature) and material variables (particle size and moisture content) can be adjusted to improve the quality of the final densified product.

Densification of ground biomass materials is still fully understood not a science, as much work is still required to fully understand how the chemical composition and physical properties, along with the process variables, impact product quality. Generating densification and compression data, along with physical and mechanical properties of a variety of biomass materials, will allow for a deeper understanding of the densification process. This in turn will result in the design of more efficient densification equipment, thus improving the feasibility of using biomass for chemical and energy production.

See: Briquetting, Pelletizing.

Deposition

Deposition is the reverse process of sublimation in which a solid is deposited from the gas phase without passing through the intermediate liquid phase.

Deposition

Gas → solid

Sublimation:

Solid → gas

In fact, there are several phase transformations that can occur when chemicals are released into the environment (Table D-2), complicating efforts to identify the original contaminant and even thwarting cleanup processes especially when the design of the cleanup process was based on knowledge of the original chemical.

Table D-2 Examples of phase transformations.

From	To	Process
Gas	Gas	N/A*
Gas	Liquid	Condensation
Gas	Solid	Deposition
Liquid	Gas	Evaporation or boiling
Liquid	Liquid	N/A*
Liquid	Solid	Freezing
Solid	Gas	Sublimation
Solid	Liquid	Melting
Solid	Solid	Transformation**

*May involve a chemical change depending upon the temperature and pressure

** For example, a change in crystal structure

See also: Evaporation, Sublimation.

Descending Bed Reactor

A descending bed system uses gravity downflow of packed solids contacted with upwardly flowing gases. The system is sometimes referred to as fixed bed reactor or moving bed reactor.

In such a reactor, combustion fumes, especially from power stations, can be cleaned prior to discharge into the atmosphere by rising through a reactor column in counter flow to the flow of a descending bed of reaction material. To ensure uniform distribution of fumes over the entire cross section of the descending bed, which is itself unobstructed by internal guides or deflectors, the conical lower section of the column consists of a series of overlapping slots between whose gaps the fumes enter – these slots may be individually adjusted for optimum fume distribution. A number of these reactors may be disposed side by side and at different vertical levels. In the reactor, the entire mass of solids descends uniformly, with no dead zones.

See also: Downflow Fixed Bed Reactor.

Desiccant Dehydrators

Desiccant dehydrators can be good alternatives to triethylene glycol systems under certain circumstances. A variety of solid desiccants are available in the market for specific applications. Some are good only for dehydrating the gas, whereas others are capable of performing both dehydration and removal of heavy hydrocarbon components. The selection of proper desiccant for a given application is a complex problem.

For solid desiccants used in gas dehydration, the following properties are desirable: (i) high adsorption capacity at equilibrium, which lowers the required adsorbent volume, allowing for the use of smaller vessels with reduced capital expenditures and reduced heat input for regeneration, (ii) high selectivity, which minimizes the undesirable removal of valuable components and reduces overall operating expenses, (iii) easy regeneration – the relatively low regeneration temperature minimizes overall energy requirements and operating expenses, (iv) good mechanical properties (such as high crush strength, low attrition, low dust formation, and high stability against aging), and (v) inexpensive, noncorrosive, nontoxic, chemically inert, high bulk density and no significant volume changes upon adsorption and desorption of water.

The most common commercial desiccants used in dry bed dehydrators are silica gel, molecular sieves, and activated alumina.

Silica gel (a generic name for a gel manufactured from sulfuric acid and sodium silicate) is a widely used desiccant, which can be used for gas and liquid dehydration and hydrocarbon recovery from natural gas. Silica gel used for natural gas drying should be stable to water. Most other silica gel types will produce fines in contact with water.

Molecular sieves are crystalline alkali metal aluminosilicates comprising a three-dimensional interconnecting network of silica and alumina tetrahedral. The structure is an array of cavities connected by uniform pores with diameters ranging from approximately 3 to 10 Å, depending on the sieve type. A molecular sieve is the most versatile adsorbent because it can be manufactured for a specific pore size, depending on the application.

There are several types of alumina available for use as a solid desiccant. Activated alumina is a manufactured or natural occurring form of aluminium oxide that is activated by heating. It is widely used for gas and liquid dehydration and will produce a dew point below -158°F. Less heat is required to regenerate alumina than for molecular sieve, and the regeneration temperature is lower.

No desiccant is perfect or best for all applications. In some applications, the desiccant choice is determined primarily by economics. Sometimes, the process conditions control the desiccant choice.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Desorption

Desorption is the reverse of adsorption whereby adsorbed matter is removed from the adsorbent.

See also: Adsorption.

Deuterium

Deuterium (symbol D or ^2H , also known as heavy hydrogen) is one of two stable isotopes of hydrogen (Table D-3). The nucleus of deuterium (sometimes referred to as a deuteron) contains one proton and one neutron, whereas the far more common hydrogen isotope, protium, has no neutron in the nucleus.

Table D-3 The Isotopes of Hydrogen.

Isotope	Description
Protium	Ordinary hydrogen with one proton and one electron in the atom. When two atoms of protium are combined with one atom of oxygen, water is created.
Deuterium	Sometimes called "heavy hydrogen," a non-radioactive isotope that has a neutron in the atom, in addition to the proton and electron. Water made with this isotope is called "heavy water."
Tritium	A radioactive isotope of hydrogen that has two neutrons in addition to the proton and the electron. Water made with this isotope is called tritium oxide. Tritium is the only one of the three hydrogen isotopes that is radioactive.

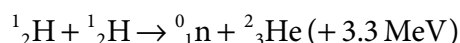
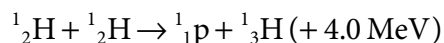
Deuterium has a natural abundance in oceans of the Earth of approximately one atom in more than six thousand (6,420) of hydrogen. Thus deuterium accounts for approximately 0.0156% (or on a mass basis 0.0312%) of all the naturally occurring hydrogen in the oceans, while the most common isotope (hydrogen-1, sometimes referred to as protium) accounts for more than 99.98%. The abundance of deuterium changes slightly from one kind of natural water.

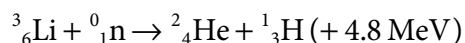
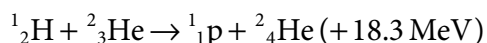
The physical properties of deuterium compounds can exhibit significant kinetic isotope effects and other physical and chemical property differences from the hydrogen analogs. Deuterium oxide (D_2O , heavy water), for example, is more viscous than common water (H_2O). Chemically, there are differences in bond energy and length for compounds of heavy hydrogen isotopes compared to normal hydrogen, which are larger than the isotopic differences in any other element. Bonds involving deuterium and tritium are somewhat stronger than the corresponding bonds in hydrogen, and these differences are enough to cause significant changes in biological reactions.

Deuterium can replace the normal hydrogen in water molecules to form heavy water (D_2O), which is approximately 10.6% denser than normal water (so that ice made from it sinks in ordinary water). Heavy water is slightly toxic in eukaryotic animals, with 25% substitution of the body water causing cell division problems and sterility, and 50% substitution causing death by cytotoxic syndrome (bone marrow failure and gastrointestinal lining failure). Prokaryotic organisms, however, can survive and grow in pure heavy water, though they develop slowly. Despite this toxicity, consumption of heavy water under normal circumstances does not pose a health threat to humans. Small doses of heavy water (a few grams in humans, containing an amount of deuterium comparable to that normally present in the body) are routinely used as harmless metabolic tracers in humans and animals.

In terms of quantum properties, the deuteron has spin +1 (triplet) and is thus a boson. The nuclear magnetic resonance (NMR) frequency of deuterium is significantly different from common light hydrogen. Infrared spectroscopy also easily differentiates many deuterated compounds, due to the large difference in infrared absorption frequency seen in the vibration of a chemical bond containing deuterium, versus light hydrogen. The two stable isotopes of hydrogen can also be distinguished by using mass spectrometry.

Deuterium and tritium are the main ingredients in most fusion reactions, and the fusion reaction deuterium and tritium into helium is only one of the possible reactions that could be the basis for the fusion power reactors of the future. The others are:





As an alternate energy source, nuclear offers several advantages over nuclear fission. One advantage is that the reserves of fusible isotopes are much larger than those of fissionable isotopes; in fact, they are essentially unlimited. Another advantage is that the products of fusion reactions are less radioactive than the products of fission reactions. Among the products of the fusion reactions listed above, only tritium and the neutrons are radioactive. The last advantage of fusion lies in its inherent safety. There would be little fusible material at any given time in the reactor, and the likelihood of a runaway reaction would thus be small. Furthermore, the reaction is so hard to achieve in the first place that small perturbations in reactor conditions would probably terminate it.

See also: Hydrogen, Nuclear Fission, Nuclear Fusion, Protium, Tritium.

Devolatilization

Devolatilization is the removal of material in the vapor phase by the action of heat either through boiling or thermal decomposition. The yield of volatile products is a function of operational conditions, including effects of reactor atmosphere gases, coal ranks, heating rates, ultimate devolatilization temperatures, pressure, residence time at ultimate temperatures, and catalysts.

An important factor of high-temperature devolatilization is the extent of secondary reactions. Higher volatile yields are obtained if the operational conditions allow secondary reactions to proceed so that coal can be degraded to tar, and tar to gaseous species. Another important factor is the reactor atmospheric gases. The two reacting gases are hydrogen and steam. A hydrogen atmosphere enhances the secondary reactions during the coal pyrolysis, and the effect of steam atmosphere is obtained because of physical processes that degrade and rupture fragments from coal and tar.

Minerals in the samples catalyze the devolatilization process by enhancing the secondary reactions by weakening chemical interactions with forming interactions between the volatile matter and mineral particles.

See also: Thermal Decomposition.

Dewatering

Dewatering is the removal of water from a carbonaceous material such as biomass by mechanical equipment such as a vibrating screen, filter, or centrifuge. Drying biomass fuel improves combustion efficiency, increases steam production, reduces air emissions, and improves boiler operation.

In a boiler or gasifier, moisture in the fuel must first be heated and evaporated, carrying with it a large quantity of heat up the stack. While a fuel dryer also consumes energy in heating and evaporating moisture, the drying is more efficient in equipment designed especially for this purpose. If heat for the dryer is recovered from the boiler flue gas or gasifier—or from other waste heat sources—efficiency is further increased. For wood chips with a moisture content on the order of 45% w/w, the maximum boiler efficiency with standard equipment is approximately 74%. If the same standard equipment is burning dry wood (on the order of 10% to 15% w/w moisture), the efficiency can be as high as approximately 80%. These efficiency improvements have corresponding steam production increases of 50% to 60%.

Thus, a biomass-fired boiler will perform better when fuel has an optimum dryness. If the fuel is too wet, it may be impossible to even keep the flame lit. With dry fuel, the flame burns hotter and more evenly, facilitating complete combustion. Also, a smaller quantity of ash is produced, reducing the cost of ash disposal. Boiler air emissions are reduced with a drier fuel, although emissions from the dryer must be considered. More complete combustion results in a lower quantity of fly ash up the boiler stack. In addition, excess air can be reduced significantly, which reduces

air velocities through the boiler and hence particulates in the flue gas. Drying biomass fuels reduces transportation costs. In addition, dry biofuels are less subject to microbiological degradation in storage.

Thus, overall efficiency can often be improved by dewatering wet feedstocks prior to thermal drying. On the downside, mechanical dewatering equipment itself can consume a large amount of energy and have high maintenance requirements, which must be weighed against the reduction in drying energy. Dewatering equipment includes drying beds, filters and screens, presses, and centrifuges. Depending on the material and the specific type of equipment, mechanical dewatering equipment may quickly reduce moisture content to as little as approximately 50%. More commonly, such a low moisture content cannot be achieved with mechanical dewatering equipment. Passive dewatering methods, such as using filter bags that are impervious to rain but allow moisture to seep out, can achieve moisture contents as low as 30% at low cost, but long periods of time – on the order of two to three months – may be required. Types of mechanical presses include belt filter presses, V-type presses, ring presses, screw presses, and drum presses. In a belt filter press, for example, the material is sandwiched between two porous belts, which are passed over and under rollers to squeeze moisture out. Belt presses are used in many industries, including wastewater treatment. A drum press consists of a perforated drum with a revolving press roll inside it that presses material against the perforated drum. This kind of press has been used with many materials, including hog fuel and bark. In a bowl centrifuge, the material enters a conical, spinning bowl in which solids accumulate on the perimeter. Belt filter presses typically have longer lives than centrifuges. Depending on the material, centrifuges can achieve lower moisture contents – on the order of 65% to 85% w/w moisture content compared to 76% to 88% w/w moisture content for belt presses when drying municipal sludge. The savings associated with achieving a lower moisture content can offset the higher first cost of a centrifuge.

The basic principles of dewatering are the same, irrespective of the type of the biomass, the size of the particles, or the machine that is being used. In every instance, a bed of particles is formed through which water and air flow under the action of a driving force. The biomass particles that comprise the bed invariably cover a wide range of sizes and composition. For example, the particles are rough and angular in shape, have an internal porosity which is full of water, often stick together, and will frequently contain a proportion of clay slime.

There are many types of dryers used in drying biomass, including direct- and indirect-fired rotary dryers, conveyor dryers, cascade dryers, and flash or pneumatic dryers. Selecting the appropriate dryer depends on many factors including the size and characteristics of the feedstock, capital cost, operation and maintenance requirements, environmental emissions, energy efficiency, waste heat sources available, available space, and potential fire hazard. Fuel dryers use superheated steam, hot air, or hot water as drying media. Air dryers derive heat from their own burners, from boiler flue gas, or from waste heat recovered from the exhaust of process heating in the facility. Water is often heated by waste heat recovery as well and can be transferred over longer distances from process equipment to the dryer than can air. Steam dryers use steam from the boiler. Dryers may be generally classified as either indirect- or direct-fired. In direct-fired dryers, flue gas or hot air is passed directly through the medium to be dried. In indirect-fired dryers, the heated medium is not passed directly through the material to be dried, but through tubes or other heat exchangers inside the dryer. Indirect-fired dryers may use flue gas or steam. Indirect dryers are well suited for drying fine and dusty materials.

Open-air drying is effective for some biomass materials, such as park trimmings or husks and stalks, can be allowed to dry naturally by storing in a covered, open area or by taking advantage of open-air solar drying. The final moisture content of air-dried materials usually varies from approximately 15% to 35%, depending on the size and characteristics of the material and ambient conditions. Open-air drying is slow and depends on weather conditions. The pile may need stirring or turning to facilitate drying. Open-air drying is generally not suitable for high water content feedstocks since they tend to decompose quickly.

In the perforated floor bin dryer, hot gases from the dryer's burner or flue gas recovered from boiler or gasifier are passed through the perforated floor into a large bin containing the feedstock. The depth of the feedstock in the dryer should not exceed 1 or 2 feet. The feedstock usually requires mixing after drying to achieve uniform moisture content.

In a rotary dryer, material is fed into a slowly rotating cylinder. Longitudinal flights inside the cylinder lift the feedstock and allow it to cascade down through the drying medium. Rotary dryers are in wide use and have a long, proven history in many industries and are the most commonly used dryer in drying hog fuel. On the other hand, high clay content paper sludges tend to ball up in a rotary dryer. Coarse bark has also been found to be problematic in rotary dryers.

Continuous-feed, direct-fired rotary dryers are the most common type of dryer for hog fuel, sawdust and bark, and many other materials. In general, the highest temperature possible without scorching the fuel results in greater dryer efficiency. An inlet temperature of around 800°F is optimum for hog fuels dried in a rotary drum direct dryer. Moisture fuels will require somewhat higher temperatures than drier fuels. But temperatures as low as 260°C (500°F) can be used with acceptable efficiencies in these dryers. Exhaust temperatures on the order of approximately 65°C (150°F) are typical. Compared to rotary steam-tube indirect-fired dryers (see below), direct-fired dryers have lower operation and maintenance costs and higher availability (i.e., less down time for maintenance). Lower-temperature dryers such as conveyor dryers and cascade dryers have several advantages over direct-fired rotary dryers. In comparison, direct-fired rotary dryers have greater emission of VOCs and particulates, lower opportunity to recover waste heat, and have greater fire hazard especially after the dryer and in shutdown. Exhaust from the dryer may need to be passed through a cyclone, baghouse filter, scrubber, or electrostatic precipitator to remove particulates.

Steam-tube dryers use steam from the power boiler to dry the fuel, passing the steam through tubes located inside the drum. Since this steam would otherwise be used to generate electricity, it does represent an energy cost. Indirect-fired dryers are less efficient than direct-fired dryers because they introduce an inefficiency associated with transferring heat from the steam tubes to the material.

In conveyor dryers, the feedstock is spread onto a moving perforated conveyor to dry the material in a continuous process. Fans blow the drying medium through the conveyor and feedstock, either upward or downward. If multiple conveyors are used, they can be in series or stacked (i.e., “multi-pass”). Conveyor dryers are very versatile and can handle a wide range of materials. They are not as commonly used in drying hog fuel but have several advantages, along with some disadvantages, compared to the more commonly used rotary dryers. Conveyor dryers are better suited to take advantage of waste heat recovery opportunities because they operate at lower temperatures than rotary dryers used in hog fuel drying.

Rotary dryers, for example, typically require inlet temperatures of at least 260°C (500°F) for drying hog fuel, but more optimally operate at approximately 425°C (800°F). In contrast, the inlet temperature of at least one commercially available vacuum conveyor dryer can be as low as approximately 5°C (10°F) above ambient, although more typically conveyor dryers operate at higher temperatures between 93 and 205°C (200 and 400°F). Because of their lower temperatures, conveyor dryers can even be used in conjunction with a boiler stack economizer to take maximum advantage of heat recovery from boiler flue gas. In this scenario, an economizer first recovers heat from the boiler flue gas. Then, exhaust from the economizer is used for fuel drying. Their lower temperature also means that there is a lower fire hazard. Emissions of volatile organic compounds (VOCs) from the dryer will also be lower.

Multi-pass conveyors, in which conveyors are arranged one above the other with material cascading down from upper conveyors to lower conveyors, save considerable space. Multi-pass dryers are common in many industries due to their small footprint and lower cost. The capital cost of conveyor dryers and rotary dryers is often comparable. However, a conveyor dryer may require less ancillary equipment for treatment of emissions, so for new installations, the overall cost may be less.

Cascade dryers have been widely used for biomass drying and can be considered of as a type of fluidized bed dryer. The material is introduced into a flowing stream of hot air in an enclosed chamber. It is carried upward by the air and then cascades back to the bottom to be lifted again. Material is drawn out through openings in the side of the chamber. Cascade dryers operate at intermediate temperatures between those of conveyor and rotary dryers. They have a smaller footprint than rotary and conveyor dryers. A disadvantage is that they are more prone to corrosion and erosion of dryer surfaces and so have higher maintenance costs.

In flash dryers (also referred to as pneumatic dryers), the feedstock is suspended in an upward flow of the drying medium, usually flue gas. Flash dryers are appropriate for drying a wide variety of materials. Flash dryers are generally cost effective only at larger scales. Electricity use by flash dryers is greater than that of other dryer types because high air flows are required to keep the material suspended. Flash dryers require a small particle size, and so shredders may be required, also increasing electrical use. Flash dryers have a small footprint.

Superheated steam dryers are similar to flash dryers, except the drying medium is steam from the boiler instead of flue gas. The steam is fed directly into the dryer, i.e., not through a heat exchanger as in steam-tube dryers. Its temperature stays above the saturation temperature, so the steam does not condense, transferring only sensible heat to the biomass. A larger quantity of steam at a lower temperature and pressure leaves the dryer than enters it. Superheated steam dryers can operate in a closed loop with low-pressure steam from the dryer being reheated and

injected back into the dryer. Since a larger quantity of steam exits the dryer, the excess must be bled off. If this excess steam is recovered for use in another process, a large fraction of the energy is recoverable. The material must be fed into the dryer by a pressure tight feeder, such as a rotary valve or plug screw feeder. Superheated steam dryers have no air emissions, no fire hazard, and a small footprint.

See also: Electrostatic Precipitator, Fabric Filters, Inertial Separator, Scrubbing – Wet Scrubbers, Unit Collectors.

Diesel-Alcohol Emulsion

Because alcohols have limited solubility in diesel, a stable emulsion must be formed that will allow it to be injected before separation occurs. Numerous techniques have been evaluated to allow for the concurrent use of diesel and ethanol in compression ignition engines. Some of these techniques include alcohol fumigation, dual injection, alcohol-diesel fuel emulsions, and alcohol-diesel fuel blends. Among these approaches, only alcohol-diesel emulsions and blends are compatible with most commercial diesel engines. Since emulsions are difficult to achieve and tend to be unstable, blends—either as micro-emulsions or using co-solvents—are the most common approach as they are stable and can be used in engines with relatively no modifications.

Blends of ethanol with diesel fuel are often referred to as E-Diesel or eDiesel or oxygenated diesel – a term that is not particularly precise since diesel blends containing methyl ester (biodiesel) or any other additive that includes oxygen can be also described as oxygenated diesel. In e-diesel blends, standard diesel fuel (such as US No. 2) is typically blended with up to 15% v/v of ethanol using an additive package that helps maintain blend stability and other properties such as the cetane number and the lubricity. The additive package may comprise from 0.2% to 5.0% v/v of the blend.

The use of e-diesel can bring some reductions in diesel PM emissions, while contradictory reports exist on its effect on nitrogen oxides, carbon monoxide, and emissions of hydrocarbon derivatives. Perhaps the biggest advantage of e-diesel is its partially renewable character, especially if renewable ethanol is used as the blending stock.

See also: Alcohols, Biodiesel, Butanol, Diesel Fuel, Ethanol, Hydroshear Emulsification Methanol, Propanol.

Diesel Cycle

The diesel cycle is the thermodynamic cycle which approximates the pressure and volume of the combustion chamber of the diesel engine. It is characterized by having constant pressure during the combustion phase, in contrast to the Otto cycle which is an idealization of the process in a gasoline engine, which approximates the real behavior with constant volume during that phase.

The maximum thermal efficiency of a diesel cycle is dependent on the compression ratio and the cut-off ratio. It has the following formula:

$$\eta_{th} = 1 - \frac{1}{r^{\gamma-1}} \left(\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)} \right)$$

In this equation, η_{th} is thermal efficiency, α is the cut-off ratio, V_3/V_2 is the ratio between the end and start volume for the combustion phase, r is the compression ratio V_2/V_1 , and γ is ratio of specific heats (C_p/C_v). This formula only gives the ideal thermal efficiency. The actual thermal efficiency will be significantly lower due to heat and friction losses. The formula is more complex than the Otto cycle (petrol/gasoline engine) relation that has the following formula:

$$\eta_{otto,th} = 1 - \frac{1}{r^{\gamma-1}}$$

The additional complexity for the diesel formula comes around since the heat addition is at constant pressure and the heat rejection is at constant volume. The Otto cycle by comparison has both the heat addition and rejection at constant volume.

Comparing the two formulae, it can be seen that for a given compression ratio (r), the ideal Otto cycle will be more efficient. However, a diesel engine will be more efficient overall since it will have the ability to operate at higher compression ratios. If a petrol engine was to have the same compression ratio, then knocking (self-ignition) would occur and this would severely reduce the efficiency, whereas in a diesel engine, the self-ignition is the desired behavior. In addition, both of these cycles are only idealizations, and the actual behavior does not divide as clearly or sharply. And the ideal Otto cycle formula stated above does not include throttling losses, which do not apply to diesel engines.

Diesel engines are more efficient than Otto cycle engines overall, but only during partial load with fuel cut-off at part of the power stroke. Unless the vehicle is at full stroke injection, it is at partial rated power. Since diesel engines use the heating effect of compressing air to ignite fuel, it can inject as little or as much fuel as the situation demands. It is important to note that Otto cycle engines can be more efficient than Diesel cycle engines only when the engine is running at or near maximum power.

See also: Diesel Engine, Diesel Fuel.

Diesel Engine

Named for the German engineer Rudolph Diesel, this internal-combustion, compression-ignition engine works by heating fuels and causing them to ignite; can use either crude oil or bio-derived fuel.

A diesel engine uses the heat of compression to initiate ignition to burn the fuel, which is injected into the combustion chamber during the final stage of compression. This is in contrast to a gasoline engine which uses the Otto cycle, in which an air-fuel mixture is ignited by a spark plug.

Diesel engines are manufactured in two-stroke and four-stroke versions. They were originally used as a more efficient replacement for stationary steam engines. Since the 1910s, diesel-powered engines have been used in submarines and ships and use in locomotives, large trucks, and electric generating plants followed later. In the 1930s, diesel engines began to be used in a few automobiles.

See: Biodiesel, Diesel Cycle.

Diesel Fuel

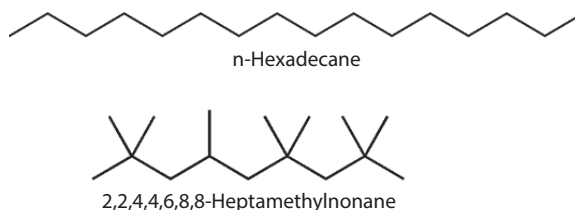
Diesel fuel is a crude oil-derived distillate fuel oil that distills between 180 and 380°C (356 to 716°F). Several grades are available depending on the use – diesel oil for diesel compression ignition (cars, trucks, and marine engines) and light heating oil for industrial and commercial uses.

Diesel fuel oil is essentially the same as furnace fuel oil, but the proportion of cracked gas oil is usually less since the high aromatic content of the cracked gas oil reduces the cetane value of the diesel fuel.

Diesel fuel was originally straight-run product obtained from the distillation of crude oil. However, with the use of various cracking processes to produce diesel constituents, diesel fuels also may contain varying amounts of selected cracked distillates to increase the volume available for meeting the growing demand. Care is taken to select the cracked stocks in such a manner that specifications are met as simply as possible.

Under the broad definition of diesel fuel, many possible combinations of characteristics (such as volatility, ignition quality, viscosity, gravity, stability, and other properties) exist. To characterize diesel fuels and thereby establish a framework of definition and reference, various classifications are used in different countries. An example is the United States in which grades No. 1-D and 2-D are distillate fuels, the types most commonly used in high speed engines of the mobile type, in medium-speed stationary engines, and in railroad engines. Grade 4-D covers the class of more viscous distillates and, at times, blends of these distillates with residual fuel oils. No. 4-D fuels are applicable for use in low- and medium-speed engines employed in services involving sustained load and predominantly constant speed.

The cetane number is a measure of the tendency of a diesel fuel to knock in a diesel engine. The scale is based upon the ignition characteristics of two hydrocarbon derivatives, viz: n-hexadecane [cetane, $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$] and 2,3,4,5,6,7,8-heptamethylnonane.



Cetane has a short delay period during ignition and is assigned a cetane number of 100; heptamethylnonane has a long delay period and has been assigned a cetane number of 15. Just as the octane number is meaningful for automobile fuels, the cetane number is a means of determining the ignition quality of diesel fuels and is equivalent to the percentage by volume of cetane in the blend with heptamethylnonane, which matches the ignition quality of the test fuel.

The manufacture of fuel oils at one time largely involved using what was left after removing desired products from crude oil. Now, fuel oil manufacture is a complex matter of selecting and blending various crude oil fractions to meet definite specifications, and the production of a homogeneous, stable fuel oil requires experience backed by laboratory control.

See: Biodiesel, Diesel Cycle, Diesel Fuel, Diesel Index.

Diesel Index

The diesel index is an approximation of the cetane number of diesel fuel calculated from the density and aniline point.

The presence of presence of paraffin hydrocarbon derivatives in diesel may be related by the aniline point which is the temperature at which aniline solubilizes the fuel in equal amount and a homogeneous mixture results. The greater the paraffin content, the higher will be the aniline point. Also, the API gravity of oil increases as the paraffin content rises. With the help of these properties, diesel index (DI) is given as:

$$\text{DI} = (\text{API} \times \text{Aniline point in } ^\circ\text{F})/100$$

The diesel index has been correlated with cetane number, and it has been found that the diesel index is directly proportional to cetane number. The cetane number is thus obtained from the diesel index. The value of diesel index should be at least 45.

See also: Cetane Index, Cetane Number.

Digester

A digester is an airtight vessel or enclosure in which bacteria decomposes biomass in water to produce biogas. There are three basic digester designs, and all of them can trap methane and reduce fecal coliform bacteria, but they differ in cost, climate suitability, and the concentration of manure solids they can digest.

A *covered lagoon digester*, as the name suggests, consists of a manure storage lagoon with a cover. The cover traps gas produced during decomposition of the manure. This type of digester is the least expensive of the three. Covering a manure storage lagoon is a simple form of digester technology suitable for liquid manure with less than 3% solids. For this type of digester, an impermeable floating cover of industrial fabric covers all or part of the lagoon. A concrete footing along the edge of the lagoon holds the cover in place with an airtight seal. Methane produced in the lagoon collects under the cover. A suction pipe extracts the gas for use. Covered lagoon digesters require large lagoon

volumes and a warm climate. Covered lagoons have low capital cost, but these systems are not suitable for locations in cooler climates or locations where a high water table exists.

A *complete mix digester* converts organic waste to biogas in a heated tank above or below ground. A mechanical or gas mixer keeps the solids in suspension. Complete mix digesters are expensive to construct and cost more than plug-flow digesters to operate and maintain. Complete mix digesters are suitable for larger manure volumes having solids concentration of 3% to 10%. The reactor is a circular steel or poured concrete container. During the digestion process, the manure slurry is continuously mixed to keep the solids in suspension. Biogas accumulates at the top of the digester. The biogas can be used as fuel for an engine-generator to produce electricity or as boiler fuel to produce steam. Using waste heat from the engine or boiler to warm the slurry in the digester reduces retention time to less than 20 days.

Plug-flow digesters are suitable for ruminant animal manure that has a solids concentration of 11% to 13%. A typical design for a plug-flow system includes a manure collection system, a mixing pit, and the digester itself. In the mixing pit, the addition of water adjusts the proportion of solids in the manure slurry to the optimal consistency. The digester is a long, rectangular container, usually built below-grade, with an airtight, expandable cover.

New material added to the tank at one end pushes older material to the opposite end. Coarse solids in ruminant manure form a viscous material as they are digested, limiting solids separation in the digester tank. As a result, the material flows through the tank in a *plug*. The average retention time (the time a manure plug remains in the digester) is 20 to 30 days. Anaerobic digestion of the manure slurry releases biogas as the material flows through the digester. A flexible, impermeable cover on the digester traps the gas. Pipes beneath the cover carry the biogas from the digester to an engine-generator set.

A plug-flow digester requires minimal maintenance. Waste heat from the engine-generator can be used to heat the digester. Inside the digester, suspended heating pipes allow hot water to circulate. The hot water heats the digester to keep the slurry at 25°C to 40°C (77°F to 104°F), a temperature range suitable for methane-producing bacteria. The hot water can come from recovered waste heat from an engine generator fueled with digester gas or from burning digester gas directly in a boiler.

Both batch and continuous digesters are commercially available. While batch systems may be suitable for some applications, they are labor intensive, and in developed countries are probably not appropriate to the steady production of gas on any significant scale. Mixing may be used in both batch and continuous digesters to enhance contact between the bacteria and substrate. It has, however, been argued that while mixing may increase conversion rates, it is not energy efficient. In two-stage systems, only the first stage is mixed. Multistage systems provide optimum conditions for the successive digestive steps, and further development may prove them to be economical for some biomass materials.

The final stage in the process is the disposal of the wastes. Essentially all the water entering the system will be present in the effluent. Direct recycle of the water after separation from the sludge cannot be practiced, as this will result in a buildup of toxic substances and eventual failure of the system. It is possible that some fraction of the water may be safely recycled, although data on this aspect have not been seen. Treatment of this large volume of water to remove the toxics is costly and is likely to be uneconomical other than in large-scale operations. It is normally assumed that the water, which is considered to have some nutritional value, will be used for irrigation. Due consideration will have to be given to the effect of trace metals and other toxic materials present, and the final disposition of the irrigated crops. The sludge, too, may be used for land application and as stated will generally have higher nitrogen content than the original material. On an absolute basis, there is, of course, less nitrogen due to losses as ammonia, and there may be additional losses on land application, as the nitrogen in the sludge is in a more volatile form. Nevertheless, the sludge resulting from the digestion of animal manure is considered to have improved fertilizer value over the original material.

Nearly all digester plants have ancillary processes to treat and manage all of the by-products. The gas stream is dried and sometimes sweetened before storage and use. The sludge liquor mixture has to be separated by one of a variety of ways, the most common of which is filtration. Excess water is also sometimes treated in sequencing batch reactors (SBRs) for discharge into sewers or for irrigation.

See: Aerobic Digestion, Anaerobic Digestion, Covered Lagoon Digester.

Digestion

Digestion is the biochemical conversion of organic material to biogas, a mixture of mainly methane and carbon dioxide. The biomass is converted by bacteria in an anaerobic environment. The energy of the biogas produced amounts 20 to 40% of the lower heating value of the feedstock.

Anaerobic digestion is a commercially proven technology and is widely used for treating wet organic wastes. Biogas can, for example, be used for firing engines. It can also be upgraded to natural gas quality and applied in grids. When used in an engine, the overall electrical conversion efficiency is on the order of 10 to 16%.

See: Aerobic Digestion, Anaerobic Digestion, Digester.

Dimethyl Ether

Due to air pollution and limited crude oil reserves, a clean alternative fuel (produced from a renewable resource) is desired. Dimethyl ether (DME), as a substitute of diesel oil and liquefied petroleum gas (LPG), is worth to be clean fuel due to its high cetane number and zero content of sulfur. Dimethyl ether can also be used as a hydrogen carrier for fuel cells, as aerosol propellants and as refrigerants. With the potential for biomass gasification technologies, synthesis of dimethyl ether from biomass as a raw material is attracting much attention. At present, the one-step synthesis of dimethyl ether from synthesis gas (STD, synthesis-gas-to dimethyl ether) has attracted attention. The main reactions included in the STD process can be depicted as follows:

Methanol Synthesis Reactions:



Methanol Dehydration Reaction:



Water Gas Shift Reaction:



With choosing equations (1) and (4) being independent reactions in methanol synthesis reactions and in combination with Equation (3) as dehydration reaction, the overall reaction for the synthesis gas to dimethyl ether process is:



These reactions form a synergistic system that allows higher syngas conversion per pass in the following manner: methanol produced by equations (1) and (2) is consumed in equation (3) to produce dimethyl ether and water; water is shifted by equation (4) to produce carbon dioxide and hydrogen which in turn are the reactants for the methanol synthesis reaction; therefore, the products of each reaction step are reactants of another step. Due to a synergy effect, thermodynamic restrictions for single pass conversion of syngas was destroyed in the synthesis gas to dimethyl ether process.

The most popular catalyst used in the dimethyl ether synthesis is usually prepared by the mechanical mixing of two components, solid acid as dehydration and Cu-based catalyst for methanol synthesis. In contrast, less effort has been spent on the agent used for dehydration of methanol.

Dehydration in the bi-functional catalyst plays an important role in dimethyl ether synthesis. Solid acid dehydrators include aluminum oxides and zeolite. Because the optional temperature for methanol synthesis usually lies

below the temperature for dehydration in the presence of γ -Al₂O₃, the Cu-based catalyst is easy to deactivate, which brings on low overall activity for the bi-functional catalyst. For this reason, extensive research has been made on using zeolite as the dehydration. Because the Si-Al ratio of zeolite will impact the number of acid sites as well as the acid strength of the catalysts, this can lead to a strong influence on the selectivity of dimethyl ether.

Dimethyl ether can be produced from a variety of biomass sources and is considered a promising substitute for diesel and liquefied petroleum gas (LPG) as it can be stored in cylinders at low pressures. However, for vehicle use, dimethyl ether attacks sealing materials (using metal to metal, graphite, Teflon). It can be used in place of diesel; its energy density is approximately 80% that of diesel, the cetane number 55-60 (46-57.8 for diesel) and zero sulfur and aromatics (environmentally friendly). In compressions ignition engines, there have been reports of lower noise levels and emissions (NO_x reductions may be further improved by end of pipe abatement).

See: Fischer Tropsch, Gasification.

Direct Biofuels

Direct biofuels are biofuels that can be used in existing unmodified diesel engines. Because engine technology changes all the time, exactly what a direct biofuel is can be hard to define; a fuel that works without problem in one unmodified engine may not work in another engine. In general, newer engines are more sensitive to fuel than older engines, but new engines are also likely to be designed with some amount of biofuel in mind.

Straight vegetable oil can be used in some (older) diesel engines. Only in the warmest climates can it be used without engine modifications, so it is of limited use in colder climates. Most commonly, it is turned into biodiesel. No engine manufacturer explicitly allows any use of vegetable oil in their engines.

Biodiesel can be a direct biofuel. In some countries, manufacturers cover many of their diesel engines under warranty for 100% biodiesel use. Many people have run thousands of miles on biodiesel without problem, and many studies have been made on 100% biodiesel. In many European countries, 100% biodiesel is widely used and is available at thousands of gas stations.

Ethanol is the most common biofuel, and over the years, many engines have been designed to run on it. Many of these could not run on regular gasoline. It is open to debate if ethanol is a direct replacement in these engines though – they cannot run on anything else. In the late 1990s, engines started appearing that by design can use either fuel. Ethanol is a direct replacement in these engines, but it is debatable if these engines are unmodified, or factory modified for ethanol.

Butanol is often claimed as a direct replacement for gasoline. It is not in widespread production at this time, and while it appears that butanol has sufficiently similar characteristics with gasoline such that it should work without any problems in any gasoline engine.

See: Biofuels, Ethanol, Methanol, Propanol And Butanol.

Direct Combustion

Direct combustion involves burning the energy crop and then using the resulting hot combustion gases to raise steam. The steam is, in turn, used to drive a steam turbine which drives a generator to produce electricity. The conversion efficiency from energy crop to energy is fairly low, especially for small systems, but this is balanced by the relatively low capital cost of direct combustion systems and the fact that the technology is tried and tested. Furthermore, using the waste heat produces much better efficiencies and economics.

Combustion facilities can burn many types of biomass fuel, including wood, agricultural residues, wood pulping liquor, municipal solid waste (MSW), and refuse-derived fuel. Combustion technologies convert biomass fuels into several forms of useful energy for commercial or industrial uses: hot air, hot water, steam, and electricity.

A furnace is the simplest combustion technology. In a furnace, biomass fuel burns in a combustion chamber, converting biomass into heat energy. As the biomass burns, hot gases are released and these gasses contain approximately 85% of the potential energy of the fuel. Commercial and industrial facilities use furnaces for heat either directly or indirectly through a heat exchanger in the form of hot air or water.

A biomass-fired boiler is a more adaptable direct combustion technology because a boiler transfers the heat of combustion into steam. Steam can be used for electricity, mechanical energy, or heat. Biomass boilers supply energy at low cost for many industrial and commercial uses.

Pile burners consist of cells, each having an upper and a lower combustion chamber. Biomass fuel burns on a grate in the lower chamber, releasing volatile gases. The gases burn in the upper (secondary) combustion chamber, and pile burners must be shut down periodically to remove ash.

Although capable of handling high-moisture fuels and fuels mixed with dirt, pile burners have become obsolete with the development of more efficient combustion designs with automated ash removal systems.

In a stationary or traveling grate combustor, an automatic feeder distributes the fuel onto a grate, where the fuel burns. Combustion air enters from below the grate. In the stationary grate design, ashes fall into a pit for collection. In contrast, a traveling grate system has a moving grate that drops the ash into a hopper.

Fluidized-bed combustors burn biomass fuel in a hot bed of granular material, such as sand. Injection of air into the bed creates turbulence resembling a boiling liquid. The turbulence distributes and suspends the fuel. This design increases heat transfer and allows for operating temperatures below 972°C (1,700°F), reducing nitrogen oxide (NO_x) emissions. Fluidized-bed combustors can handle high-ash fuels and agricultural biomass residue.

Conventional combustion equipment is not designed for burning agricultural residues. Straw and grass contain alkali (potassium and sodium) compounds, which are also present in all annual crops and crop residues and in the annual growth of trees and plants. During combustion, alkali combines with silica, which is also present in agricultural residues. This reaction causes slagging and fouling problems in conventional combustion equipment designed for burning wood at higher temperatures.

Volatile alkali lowers the fusion temperature of ash. In conventional combustion equipment having furnace gas exit temperatures above 790°C (1,450°F), combustion of agricultural residue causes slagging and deposits on heat transfer surfaces. Specially designed boilers with lower furnace exit temperatures could reduce slagging and fouling from combustion of these fuels. Low-temperature gasification may be another method of using these fuels for efficient energy production while avoiding the slagging and fouling problems encountered in direct combustion.

Combustion facilities that produce electricity from steam-driven turbine-generators have a conversion efficiency on the order of 17 to 25%. Using a boiler to produce both heat and electricity (cogeneration) improves overall system efficiency to as much as 85%. That is, cogeneration converts 85% of the fuel's potential energy into useful energy in two forms: electricity and steam heat.

Two cogeneration arrangements, or cycles, are possible for combining electric power generation with industrial steam production. Steam can be used in an industrial process first and then routed through a turbine to generate electricity. This arrangement is called a bottoming cycle. In the alternate arrangement, steam from the boiler passes first through a turbine to produce electric power. The steam exhaust from the turbine is then used for industrial processes or for space and water heating. This arrangement is called a topping cycle.

The direct-fired gas turbine is another combustion technology for converting biomass to electricity. In this technology, fuel pretreatment reduces biomass to a particle size of less than 2 millimeters and a moisture content of less than 25%. Then, the fuel is burned with compressed air. Cleanup of the combustion gas reduces particulate matter before the gas expands through the turbine stage. The turbine drives a generator to produce electricity.

Co-firing biomass as a secondary fuel in a coal-burning power plant using high-sulfur coal could help reduce sulfur dioxide and nitrogen oxide emissions. Also, co-firing decreases net carbon dioxide emissions from the power plant (if the biomass fuel comes from a sustainable source). Co-firing may require wood fuel preparation or boiler modifications to maintain boiler efficiency.

See: Combustion.

Direct-Fired Biomass

The technologies for the conversion of biomass for electricity production are direct combustion, gasification, and pyrolysis.

Direct combustion (Figure 1) involves the oxidation of biomass with excess air, producing hot flue gases which in turn produce steam in the heat exchange sections of boilers. The steam is used to generate electricity in a Rankine

cycle; usually, only electricity is produced in a condensing steam cycle, while electricity and steam are cogenerated in an extracting steam cycle. Currently, biomass-fired steam cycle plants typically use single-pass steam turbines.

However, in the past decade, efficiencies and more complex design features, characteristic previously of only large-scale steam turbine generators (>200 MW), have been transferred to smaller capacity units. Current biomass designs include reheat and regenerative steam cycles as well as supercritical steam turbines. The two common boiler configurations used for steam generation with biomass are stationary- and traveling-grate combustors (stokers) and atmospheric fluid-bed combustors.

See: Combustion.

Dispersion

The dispersion of chemicals into the environment can occur in three ways: (i) dispersion during combustion processes, such as fuel conversion or waste incineration: chemicals released include polycyclic aromatic hydrocarbon derivatives, dioxin derivatives, and furan derivatives, (ii) dispersion after the unintentional release of chemicals following accidents or by slow leakage such as the release of polychlorinated biphenyl derivatives from electrical installations, and (iii) the intentional dispersion of chemicals as, for example, during the use of pesticides and other agricultural chemicals.

Thus, the disposal of a chemical into a water course and subsequent transportation of the chemical are referred to as dispersion. This is often a result of water surface turbulence, but also may result from the application of chemical agents (dispersants). The dispersed chemicals may remain in the water column or coalesce with other chemicals (the same chemical or different chemicals) and gain enough energy to be adsorbed by minerals, soil, or sediment.

In the context of the geosphere, dispersion is a process that occurs in soil that is particularly vulnerable to erosion by water. In a soil layer where clay minerals are saturated with sodium ions (*sodic soil*), the soil can break down very easily into fine particles and wash away. This can lead to a variety of soil and water quality problems, including: (i) large losses of soil losses by gully erosion and tunnel erosion, (ii) structural degradation of the soil, clogging, and sealing where dispersed particles settle, and (iii) turbidity in water due to suspended soil particles which also cause transportation of nutrients from the land. Dispersive soil is more common in older landscapes where leaching and illuviation processes have had more time to show an effect.

Briefly, gully erosion involves creation of a gully created by running water, eroding sharply into soil and typically occurs on a hillside. On the other hand, tunnel erosion occurs in some soils where channels and tunnels develop beneath the surface. It is insidious as it is not readily noticeable (apart from small sediment fans at the tunnel discharge point) until the surface itself is undermined. Illuvium is material displaced across a soil profile, from one layer to another one, by the action of rainwater.

The dispersion of chemicals released into the environment has been the focus of much attention because of the realization that the dispersion behavior of chemicals can be markedly different when different chemicals are considered. Accidents that involve chemicals give rise to a new class of problems in dispersion prediction for the following reasons: (i) the material is, in almost all cases, stored as a solid but may also emit a gas after a spill and exposure to the air, (ii) the modes of release can vary widely and geometry of the source can take many forms and the initial momentum of the spill may be significant, (iii) in some cases, a chemical transformation also takes place as a result of reaction with water vapor in the ambient atmosphere.

Emissions of many chemicals of concern occur into the air initially, from where they are dispersed into other media. Many chemicals emitted into the air, for instance from combustion processes, tend to become associated with particulate matter. Removal from the air occurs through a range of complex processes involving photodegradation, and particle sedimentation and/or precipitation (known respectively as *dry deposition* and *wet deposition*). Chemicals may undergo several cycles of physical and/or chemical transformation which can also make chemicals more accessible to photochemical or biodegradation.

In addition, the physical properties of the chemical may result in one or more interactions with the surrounding ecosystem, especially if the chemical is reactive and has the potential to react quickly with the air, water, or soil. This reactivity will influence the dispersability of the chemical, and, moreover, if the release occurs over a short time scale, compared to the steady-state releases characteristic of many chemical release problems, this can give rise to the

complication of predicting dispersion for time varying releases. There is also the uncertainty of individual predictions resulting from variability related to the behavior of a mixture. Also, the dispersing chemical, which is typically denser than air, may form a low-level cloud that is sensitive to the effects of either natural or man-made obstructions in the surrounding topography.

Wind transport (Aeolian transport – relocation by wind) can also occur and is particularly relevant when dust from solids (even coke dust which contains deposited chemicals) and catalyst dust are also considered. Dust becomes airborne when winds traversing arid land with little vegetation cover pick up small particles such as catalyst dust, coke dust, and other debris and send them skyward after which the movement of pollutants in the atmosphere is caused by transport, dispersion, and deposition. Dispersion results from local turbulence, that is, motions that last less than the time used to average the transport. Deposition processes, including precipitation, scavenging, and sedimentation, cause downward movement of pollutants in the atmosphere, which ultimately move the pollutants back to the ground surface but not necessary in the locals from which the pollutants originated.

Dissolution

Dissolution is the process whereby chemicals (such as gases, liquids, or solids) dissolve into a liquid (such as water or another solvent) by which these chemicals in the original state (gas, liquid, or solid) become a solute (dissolved component), forming a solution of the gas, liquid, or solid in the original solvent. On the other hand, solid solutions are the result of dissolution of one solid into another (such as metal alloys) and occur where the formation is governed and described by the relevant phase diagram. In the case of a crystalline solid dissolving in a liquid, the crystalline structure must be disintegrated such that the separate atoms, ions, or molecules are released. For liquids and gases, the molecules must be able to form non-covalent intermolecular interactions with those of the solvent for a solution to form. Dissolution is of fundamental importance in all chemical processes, especially the solubility of chemicals in water which can be enhanced by the occurrence of acid rain.

Generally, many chemicals (especially the inorganic chemicals) are polar and are usually soluble in water but insoluble in organic solvents (such as diethyl ether, dichloromethane, chloroform, and hexane). The solubility (dissolution) characteristics of chemical species in water is complex and very much dependent upon the structure and properties of the chemical(s). The chemical may be a gas, a liquid, or a solid (the solute) that dissolves in water – the solubility depends on the physical and chemical properties of the chemicals as well as on temperature, pressure, and the pH (acidity or alkalinity of the water).

Furthermore, the extent of solubility of the chemical can range from infinitely soluble (without limit) to poorly soluble (such as some lead salts) – the term *insoluble* is often applied to poorly or very poorly soluble compounds, and (in the world of chemistry) a common threshold to describe a chemical as insoluble is a solubility less than 0.1 g per 100 mL of water. However, solubility of a chemical in water should not be confused with the ability of water to dissolve the chemical because apparent solubility of the chemical might also occur because of a chemical reaction (*reactive solubility*).

Solubility of a chemical in water applies not only to environmental chemistry but to areas of chemistry, such as (alphabetically): biochemistry, geochemistry, chemistry, and physical chemistry. In all cases, the solubility of the chemical depends on the physical conditions (temperature, pressure, and concentration of the chemical) and the enthalpy and entropy relating to the water and the chemicals concerned. Water is, by far, the most common solvent in chemistry and is a solvent for a wide range of chemicals, especially those chemicals that readily form ions. This is a crucial factor in which acidity and alkalinity play a role as in much of the area known as environmental chemistry.

In addition, the term *dissolved chemicals* (or *total dissolved solids*) is used as a broad classification for chemicals of varied origin and composition within aquatic systems (the aquasphere). The source of the dissolved chemical in freshwater systems and in marine systems depends on the body of water. When water comes into contact with highly ionizable chemicals, these chemicals can drain into rivers and lakes as a dissolved chemical. Whatever the source of the dissolved chemical, it is also extremely important in the transport of metals in aquatic systems – certain metals can form extremely strong metallic complexes with a dissolved solute which enhances the solubility of the metal in aqueous systems while also reducing the bioavailability of the metal.

In terms of chemicals that do not occur naturally in the environment, knowledge of the structure and properties can be used to examine relationships between the solubility properties of the chemical and its structure, and vice versa. In fact, structure dictates function which means that by knowing the structure of a chemical, it may be (but not always) possible to predict the properties of the chemical such as its solubility, acidity or basicity, stability, and reactivity. In the context of environmental distribution of a chemical, predicting the solubility of a molecule is a useful component of knowledge.

Dissolved chemicals are generally associated with the various characteristics of drinking water (such as taste, smell, color, and odor), and the quality of drinking water, as perceived by the senses, largely determines the acceptability of water. For health-related contaminants – a contaminant that is unsafe for one species of flora or fauna should be considered unsafe for all, until proven otherwise – the general characteristics (taste, smell, and odor) are subject to social, economic, and cultural considerations.

On the other hand, the presence of (non-dissolved) suspended solids in water gives rise to turbidity. Suspended solids may consist of clay, silt, airborne particulates, colloidal organic particles, plankton, and other microscopic organisms. The presence of particulate matter in water may not only be offensive to the general senses but can also, in a more serious aspect, protect bacteria and viruses from the action of disinfectants. In addition, the adsorptive capacity of some suspended particulates can lead to entrapment of undesirable inorganic compounds and organic compounds present in the water and in this way, turbidity can bear an indirect relationship to the health aspects of water quality.

See also: Water.

Distillation

Distillation has remained a major process for the separation of mixtures for several centuries, in particular for the separation of mixtures containing volatile organic compounds. The process consists of heating a liquid to its boiling point, separating the vapors from the liquid, and then condensing the vapors to form a new liquid phase, and the condensate contains a higher concentration of the more volatile component than did the original feedstock. If the difference in boiling point between the components of the feed is large, it may be possible to achieve the desired purification in a simple apparatus. On the other hand, if the difference is only a few degrees, a satisfactory separation may require a complex apparatus and a lot of energy. Fortunately, many of the distillations encountered in biomass conversion to liquids and also in waste disposal involve differences in boiling point between the components in the feed. Thus, the components in the feed can usually be separated in a single-stage batch still. The range of liquids that can be distilled runs from liquefied gases at low temperatures and/or high pressure up to high boiling liquids under vacuum just below their thermal decomposition temperature.

Generally, the maximum permissible temperature (in the vaporizing furnace or heater) to which the feedstock can be subjected is 350°C (660°F). The rate of thermal decomposition increases markedly above this temperature, although higher temperatures (up to approximately 395°C, 745°F) are part of the specifications for some distillation units – serious cracking does not occur at these higher temperatures but is subject to the properties of the crude oil feedstock and the residence time of the feedstock in the hot zone. If unplanned cracking occurs within a distillation unit, coke deposition can occur in the heater pipes or in the tower itself, resulting in failure of the distillation unit. In the modern sense, distillation was the first method by which crude oil-based fuels were refined.

Batch Distillation

The batch distillation process consists of placing a quantity of feedstock in a vessel, heating it to generate vapors, and then condensing the vapors in a separate vessel or condenser by cooling them to below their condensing temperature. The condensed vapors are the distillate, or overhead, and the residue left in the boiler when the distillation is finished is called the still bottoms or residue.

In the simplest form, a batch still is the combination of a boiler and condenser. However, it can also have large numbers of vapor-liquid contacting stages inserted between the boiler and the condenser in the form of a distillation column or tower. This greatly increases the composition difference between the distillate and the contents of the boiler and makes the separation much sharper. However, when this type of still is started, it must be run at total

reflux for several hours before starting to collect product which allows time for the concentration gradient to be established in the column.

Continuous Distillation

Continuous distillation is the process in which the feedstock is continuously fed to the distillation apparatus by either gravity flow or by means of a suitable pump along with flow rate control to provide the continuous feed. The continuous distillation process can vary in complexity from a simple one-stage equilibrium flash separation to a compound column having many enriching and stripping stages in a single apparatus. The equilibrium flash is generally used where the separation is achieved because of a substantial difference in volatility between the components to be separated. It is also useful when a small amount of relatively volatile material must be removed from a large amount of higher boiling material.

Multistage distillation is usually used to separate and recover materials which have relatively close boiling points, that is, less than 20°F apart. Typical continuous multistage separations can use enriching columns, stripping columns, or compound columns. Enriching columns are used to recover high purity lower boiling products from higher boiling point mixtures. In contrast, stripping columns are used to remove lighter materials from heavier products that are desired in high purity.

Distillation at Atmospheric Pressure

Distillation columns are the most commonly used separation units in a refinery. Operation is based on the difference in boiling temperatures of the liquid mixture components, and on recycling counter-current gas-liquid flow. The temperature distribution up the column results in different mixture compositions at different heights. While multi-component inter-phase mass transfer is a common phenomenon for all column types, the flow regimes are different depending on the internal elements used. The two main types are a tray column and a packed column, the latter equipped with either random or structured packing. Different types of distillation columns are used for different processes, depending on the desired liquid holdup, capacity (flow rates), and pressure drop, but each column is a complex unit, combining many structural elements.

Heat exchangers are also used to preheat the feedstock before it enters the furnace. These exchangers are bundles of tubes arranged within a shell so that a stream passes through the tubes in the opposite direction of a stream passing through the shell. Thus, cold crude oil, by passing through a series of heat exchangers where hot products from the distillation tower are cooled, before entering the furnace and saving of heat in this manner, may be a major factor in the economical operation of refineries.

Steam reboilers may take the form of a steam coil in the bottom of the fractional distillation tower or in a separate vessel. In the latter case, the bottom product from the tower enters the reboiler where a part is vaporized by heat from the steam coil. The hot vapor is directed back to the bottom of the tower and provides part of the heat needed to operate the tower. The non-volatile product leaves the reboiler and passes through a heat exchanger, where its heat is transferred to the feed to the tower. Steam may also be injected into a fractional distillation tower not only to provide heat but also to induce boiling to take place at lower temperatures. Reboilers generally increase the efficiency of fractionation, but a satisfactory degree of separation can usually be achieved more conveniently by the use of a *stripping* section. The *stripping operation* occurs in that part of the tower below the point at which the feed is introduced. The more volatile components are stripped from the descending liquid. Above the feed point (the rectifying section), the concentration of the less volatile component in the vapor is reduced.

Distillation at Reduced Pressure

The boiling range of the highest boiling fraction that can be produced at atmospheric pressure is limited by the temperature at which the residue starts to decompose or *crack*. If the atmospheric residuum is required for the manufacture of lubricating oils, further fractionation without cracking may be desirable, and this may be achieved by distillation under vacuum. The residua produced by distillation under reduced pressure have properties markedly different from the residua produced by distillation at atmospheric pressure.

In the vacuum tower, the feedstock is charged through a heater into the vacuum column in the same manner as whole crude is charged to an atmospheric distillation unit. However, whereas the flash zone of an atmospheric column may be at 14 psi to 18.5 psi (760-957 mm), the pressure in a vacuum column is very much lower, generally

less than 0.8 psi (less than 40 mm Hg) in the flash zone to less 0.2 psi (less than 10 mm Hg) at the top of the vacuum tower. The vacuum heater transfer temperature is generally used for control, even though the pressure drop along the transfer line makes the temperature at that point somewhat meaningless. The flash zone temperature has much greater significance.

The distillation of high-boiling feedstocks may require pressures as low as 0.29-0.58 psi (15-30 mm Hg), but operating conditions are more usually 0.97-1.93 psi (50-100 mm Hg). Volumes of vapor at these pressures are large, and pressure drops must be small to maintain control, so vacuum columns are necessarily of large diameter. Differences in vapor pressure of different fractions are relatively larger than for lower boiling fractions, and relatively few plates are required. Under these conditions, a heavy gas oil may be obtained as an overhead product at temperatures of approximately 150°C (300°F). Lubricating oil fractions may be obtained as sidestream products at temperatures of 250 to 350°C (480 to 660°F). The feedstock and residue temperatures being kept below the temperature of 350°C (660°F), above which the rate of thermal decomposition (cracking) increases. The partial pressure of the hydrocarbons is effectively reduced yet further by the injection of steam. The steam added to the column, principally for the stripping of bitumen in the base of the column, is superheated in the convection section of the heater.

See also: Evaporation, Extraction.

Distribution in the Environment

The movement of released chemicals into the Earth systems is caused by transport, dispersion, and deposition of the chemicals (or, in some cases transformed chemicals). Transport is movement caused by a time-averaged flow while dispersion results from local factors and deposition processes, including precipitation, scavenging, and sedimentation which ultimately move (for example) atmospheric chemical pollutants to the water and land surfaces of the Earth.

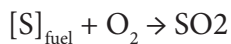
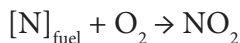
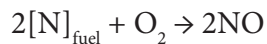
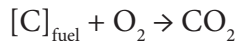
Furthermore, the distribution of chemical in the environment is influenced by the physical properties of the chemicals and the minerals (such as the clay minerals) with which the chemicals come into contact. However, the movement of chemicals through the environment is complex and is difficult to predict. Different types of chemicals react differently with soils, sediments, and other geologic materials and commonly travel along different flow paths and at different velocities. For example, using soil as the example, contaminants that are highly soluble, such as salts (e.g., sodium chloride, NaCl) move readily from surface soils to saturated materials below the water table. This often occurs during and after rainfall events.

Other contaminants that are not highly soluble may have considerably longer residence times in the soil zone. Some contaminants adsorb readily onto soil particles and slowly dissolve during precipitation events, resulting in dissolved fraction concentrations of contaminants migrating to groundwater. Once below the water table, chemicals are also subject to dispersion (mechanical mixing with uncontaminated water) and diffusion (dilution by concentration gradients).

Typically, chemicals released from various sources are ultimately dispersed among, and can at times accumulate in, various environmental compartments (such as soil as well as various floral and faunal species). Some contaminants may contribute primarily to environmental compartments on a local scale, but other contaminants that are more persistent in the environment can be distributed over much greater distances – even up to a regional scale, a national scale, or an international scale.

Thus, understanding the potential environmental impact of dispersed chemicals requires an understanding of the relative contribution of the various sources of the pollutants as well as the types of the and the potential for a pollutant to undergo chemical (or physical) transformation in the environment. Therefore, an investigation of a potential contaminant must account for transport of the contaminant through ecosystems. The required characterization of concentrations of contaminants in an environmental medium, such as air, involves accounting for the gains (or inputs to) and losses from that medium, and transport through it.

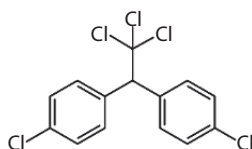
Some examples of atmospheric pollutants include nitrogen dioxide (NO₂), sulfur dioxide (SO₂), and carbon monoxide (CO). The first two pollutants combine with water to form acids, which not only irritate the lungs but also contribute to the long-term destruction of the environment due to the generation of acid rain.



Carbon monoxide, generated by the incomplete combustion of hydrocarbons, displaces and prevents oxygen from binding to hemoglobin and causes asphyxiation. Also, it binds with metallic pollutants and causes them to be more mobile in air and water.

Fresh, clean, and drinkable water is a necessary but limited resource on the planet. Industrial, agricultural, and domestic wastes can contribute to the pollution of this valuable resource, and water pollutants can damage human and animal health. Three important classes of water pollutants are heavy metals, pollutants, and organic pollutants. Heavy metals include transition metals such as cadmium, mercury, and lead, all of which can contribute to brain damage. pollutants like hydrochloric acid, sodium chloride, and sodium carbonate change the acidity, salinity, or alkalinity of the water, making it undrinkable or unsuitable for the support of floral and faunal species.

The use of pesticides (such as phosphates) in agriculture contributes to environmental pollution. Pesticides are used to control the growth of insects, weeds, and fungi, which compete with humans in the consumption of crops. This use not only increases crop yields and decreases grocery prices, but also controls diseases such as malaria and encephalitis. However, the spraying of crops and the water runoff from irrigation transports these harmful chemicals to the habitats of nontarget animals. Chemicals can build up in the tissues of these animals, and when humans consume the animals, the increased potency of the pesticides is manifested as health problems and in some cases death. Chemists have recently developed naturally occurring pesticides that are toxic only to their particular targets and are benign to birds and mammals. The most significant pesticide of the twentieth century was DDT (dichloro-diphenyl-trichloroethane), which was highly effective as an insecticide but did not break down in the environment and led to the death of birds, fish, and some humans.



DDT

In order to take account of the multimedia nature of pollutant transport, assessments usually examine multiple pathways that define the movement of a pollutant from a source, through a linear sequence of environmental compartments, to a receptor. An example of a particular pathway is a source emitting a pollutant to air (an air compartment), transport of the pollutant to the air above a field (another air compartment), deposition on vegetation (a vegetation compartment), eating of the vegetation by cows (an animal compartment), and drinking by humans of the milk from cows (a receptor, exposed by the ingestion route). The pathway may be elaborated to almost any arbitrary degree, depending on how it is to be evaluated. For example, the deposition of a pollutant from air to vegetation may incorporate additional air compartments like a boundary layer of air around the vegetation, and the laminar flow layer of air above the vegetation.

The most appropriate method for assessing the environmental transport of a specific substance depends on the linearity of the physical and chemical processes involved in pollutant transport with respect to pollutant concentrations in each compartment—fluxes between compartments usually depend linearly on the concentrations in connected compartments. If this linearity holds, a transport network through multiple compartments may be represented by the linear super-position of non-self-intersecting pathways. Where nonlinearities occur, the approach becomes less useful, and all compartments may have to be examined simultaneously, although it sometimes may be possible to contain all the nonlinearities within the more complex components of single pathways.

To effectively monitor changes in the environmental behavior of chemicals that are of most concern, it is extremely important to understand how these chemicals typically behave in natural systems and in specific ecosystems. Equally important is an understanding of how these chemicals might respond to specific best management practices. Some of the discharged chemicals only become problems at high concentrations that impair the beneficial uses of these ecosystems. An effective monitoring program explicitly considers how these chemicals may change as they move from a source into the groundwater, surface water, or into the soil. This includes an understanding of how a specific chemical may be introduced or mobilized within an ecosystem, how the chemical moves, or through an ecosystem, the transformations that may occur during this process.

As an example, groundwater will normally look clear and clean because the ground naturally filters out particulate matter. However, natural and manufactured chemicals can be found in groundwater. As groundwater flows through the ground, metals such as iron and manganese are dissolved and may later be found in high concentrations in the water. Industrial discharges, urban activities, agriculture, groundwater pumpage, and disposal of waste all can affect groundwater quality. Pollutants can be anthropogenic in origin such as chemicals from leaking fuel tanks or toxic chemical spills. Pesticides and fertilizers applied to lawns and crops can accumulate and migrate to the water table. Also, leaks from septic tanks and/or waste disposal sites can introduce bacteria to the water, and pesticides and fertilizers that seep into farmed soil can eventually end up in water drawn from a well. On the other hand, a well might have been placed in land that was once used for something like a garbage or chemical dump site.

However, the entry of chemicals into the environment and the distribution of these chemicals within the environment are often complex, and there have been many occasions when a significant amount of a chemical (or a mixture of chemicals) has entered an ecosystem and the effects of contamination are well defined. Generally, the assumption is that the chemical (or a mixture thereof) does not rapidly diffuse away, but remains in the immediate vicinity at a noticeably high concentration or perhaps moves, but in such a way that concentration levels of the chemical remain high as it moves. Such cases would normally occur when large quantities of a substance were being stored, transported, or otherwise handled in concentrated form. Thus, due to leakages, spills, improper disposal, and accidents during transport, compounds that have become subsurface contaminants that threaten various.

Background knowledge of the sources, chemistry, and potential risks of toxic heavy metals in contaminated soils is necessary for the selection of appropriate remedial options. Remediation of soil contaminated by heavy metals is necessary to reduce the associated risks, make the land resource available for agricultural production, enhance food security, and scale down land tenure problems. Immobilization, soil washing, and phytoremediation are frequently listed among the best available technologies for cleaning up heavy metal contaminated soils. These technologies are recommended for field applicability and commercialization in the developing countries also where agriculture, urbanization, and industrialization are leaving a legacy of environmental degradation.

Finally, there are methods that can be used to calculate factors available that can be used to understand the entry of chemical in the environment and the method of dispersal. For example, the amount of a pollutant available for exposure depends on its persistence and the potential for its bioaccumulation as well as the exposure route.

By way of explanation, an exposure route refers to the way that a released chemical enters the flora and fauna as a result of the release. The route of the potential uptake of the chemical is an important attribute of an exposure event.

In addition, any chemical (including both organic chemicals and inorganic chemicals) that is introduced into the environment can be considered to be capable of accumulation (or bioaccumulation) if the chemical has a degradation

half-life in excess of thirty days or if the chemical has a bioconcentration factor (BCF) greater than 1,000 or if the $\log K_{ow}$ (the octanol-water partition coefficient of the chemical) is greater than 4.2:

$$BCF = (\text{concentration in biota})/(\text{concentration in ecosystem})$$

The octanol/water partition coefficient (K_{ow}) is the ratio of the concentration of a chemical in the octanol phase relative to the concentration of the chemical in the aqueous phase of a two-phase octanol/water system:

$$K_{ow} = (\text{concentration in octanol phase})/(\text{concentration in aqueous phase})$$

The bioconcentration factor (BCF) indicates the degree to which a chemical may accumulate in biota (flora and fauna). However, measurement of bioconcentration is typically made on faunal species and is distinct from transport in the food chain, bioaccumulation, or biomagnification. The bioconcentration factor is a constant of proportionality between the chemical concentration in flora or fauna in an ecosystem. It is possible, for many chemicals, to estimate the bioconcentration factor from the octanol-water partition coefficients (K_{ow}):

$$\text{Log}(\text{bioconcentration factor}) = m\log K_{ow} + b$$

In terms of actual numbers, for many lipophilic chemicals, the bioconcentration factor can be calculated using the regression equation:

$$\log BCF = -2.3 + 0.76 \times (\log K_{ow})$$

Furthermore, empirical relationships between the octanol-water partition coefficients and the bioconcentration factor can be developed on a chemical-by-chemical basis.

Indeed, an analysis of the amount of chemical waste formed in processes for the manufacture of a range of fine chemicals and chemical intermediates has revealed that the amount of waste generated in some processes may be in excess of the amount of the desired product and such overproduction of waste was not exceptional in the chemical industry. As a means of measuring the amount of waste vis-à-vis the amount of products, the E-factor (environmental factor) (kilograms of waste per kilogram of product) was introduced as an indication of the environmental footprint of the manufacturing process in various segments of the chemical industry. This factor is derived from the chemicals and fine chemicals industries as a measure of the efficiency of the manufacturing process: Thus, simply:

$$E = \text{kilograms of waste/kilogram of product}$$

The factor can be conveniently calculated from a knowledge of the number of tons of raw materials purchased and the number of tons of product sold, the calculation being for a particular product or a production site or even a whole company. A higher E-factor means more waste and, consequently, a larger environmental footprint – thus, since mass cannot be created resulting in a negative E-factor, the ideal E-factor for any process is zero.

However, in the context of environmental protection and to be all inclusive, the E-factor is the total mass of raw materials plus ancillary process requirements minus the total mass of product, all divided by the total mass of product. Thus, the E-factor should represent the *actual amount* of waste produced in the process, defined as everything but the desired product and takes the chemical yield into account and includes reagents, solvent losses, process aids, and (in principle) even the fuel necessary for the process. Moreover, use of the E-factor has been widely adopted by many of the chemical industries and the pharmaceutical industries in particular. Thus, a major aspect of process development recognized by process chemists and by process engineers is the need for determining an E-factor – whether or not it is called by that name (i.e., the E-factor), but *chemicals in compared to chemical out* has become a major yardstick in many of the chemicals industries.

In terms of properties and transportation of the chemical, particulate matter occupies a somewhat different place to the more conventional chemical contaminants insofar as the transport characteristics of particles depend on the particle size. Fine and coarse particles in ambient air differ in their chemical composition, solubility, acidity, sources and formation processes, atmospheric lifetime, infiltration indoors, and transport distances. Most airborne particles are quite small (less than $0.1\text{ }\mu\text{m}$ in diameter, $0.2\text{ }\mu\text{m}$; $1\text{ }\mu\text{m} = 1\text{ meter} \times 10^{-6}$), but most of the particle volume (and mass) is found in particles with diameters greater than $0.1\text{ }\mu\text{m}$. The size distribution of airborne particles is often multimodal.

Fine particles are usually defined as those having an aerodynamic diameter less than $2.5\text{ }\mu\text{m}$. Fine and coarse particles generally have distinct sources and formation mechanisms, although there may be some overlap. Fine particles are usually formed from gases in two ways: (i) nucleation, which involves the formation of new particles from low vapor pressure chemicals present in vapor form, produced either from combustion or from chemical reaction of gases and (ii) condensation of gases onto existing particles. Particles formed from nucleation also coagulate to form relatively larger particles, although particles normally do not grow above $1.0\text{ }\mu\text{m}$ in aerodynamic diameter by these processes.

Particles formed as a result of the chemical reaction(s) of gases (which are secondary particles because the direct emission from a source is a gas such as sulfur dioxide, SO_2 , or nitric oxide, NO) that is subsequently converted to a low vapor pressure substance (such as sulfuric acid or nitric acid) that subsequently nucleates or condenses. Examples include sulfates, some low volatile organic compounds, and ammonium salts.

Such transformations can take place locally, during prolonged stagnations of ambient air, or during transport over long distances, and are affected by moisture, sunlight, temperature, and the presence or absence of fogs and clouds. In general, particles formed from these types of secondary processes will be more uniform in space and time than those that result from primary emissions. Particles directly emitted by sources, referred to as primary particles, are also found in the fine particle fractions (the most common being particles from combustion sources that are less than $1.0\text{ }\mu\text{m}$ in aerodynamic diameter). In contrast to fine particles, most of the coarse particle fraction of ambient aerosol originated as particles emitted directly to the atmosphere, and some particles generated during combustion processes, such as fly ash and soot, might also be found in the coarse fraction.

Every particle in the atmosphere tends to settle to the ground through the effects of gravity, but the tendency to settle is opposed or abetted by other effects including electrostatic and aerodynamic forces. The outcome is that particles deposit to the ground at velocities that depend primarily on their particle diameter and density. For coarse particles, controlled primarily by gravity, the deposition velocity is proportional to the square of the particle diameter. For fine particles, deposition is controlled more by electrostatic and other effects than by gravity, so that they deposit more rapidly than would be expected from gravity and their size alone. The result is that fine particles with an aerodynamic diameter between 0.1 and $1.0\text{ }\mu\text{m}$ have the minimum deposition velocity of particles. Such fine particles will remain suspended for much longer times (on the order of days to weeks for fine particles as opposed to minutes to hours for coarse particles) and will travel much farther (as far as thousand miles) than the coarse particle fraction.

See also: Absorption, Adsorption, Dispersion, Dissolution, Emulsification, Evaporation, Leaching, Sedimentation, Spreading, Sublimation.

Domestic Waste

Waste is the remains or by-product from a process for which no use is planned or foreseen. The words domestic (or municipal) and industrial are qualifiers of the source of the waste and, to some extent, also descriptive of the contents of the waste. Once a material has been designated as waste, it remains waste until it has been fully recovered and no longer poses a potential threat to the environment.

Thus, domestic waste (also known as rubbish, garbage, trash, or junk) is unwanted or undesired material. Waste is the general term; though the other terms are used loosely as synonyms, they have more specific meanings: rubbish or trash are mixed household waste including paper and packaging; food waste or garbage (North America)

is kitchen and table waste; and junk or scrap is metallic or industrial material that contribute to organic waste (Table D-4).

Table D-4 Examples of the types of organic chemical waste.

Source	Waste type
Chemical manufacturing	Spent solvents
	Reactive materials
Cleaning agents	Spent solvents
Construction industry	Spent solvents
Cosmetics manufacturing	Ignitable materials
	Flammable solvents
Crude oil recovery and refining	Drilling mud spills
	Spilled solvents
	Process sludge
Furniture manufacturing and refinishing	Ignitable materials
	Spent solvents
Leather products	Waste solvents
Power generation	Gases and coal dust
	Combustion waste (ash and slag)
Printing industry	Spent solvents
Vehicle maintenance	Ignitable materials
	Spent solvents

There are other categories of waste as well: sewage, ash, manure, and plant materials from garden operations, including grass cuttings, fallen leaves, and pruned branches.

See: Industrial Waste, Waste.

Downdraft Combustion

Down-draught combustion is a method of controlling the emission of smoke which involved inversion of the simple coal fire. Air enters at the top of the container, and combustion products leave at the bottom; an important technical feature is that the flame front travels in the opposite direction of the primary air. In this type of system, volatile matter which was evolved ahead of the flame front would be swept back by the air stream through the flame and into the incandescent part of the bed, where it is combusted thereby reducing its contribution to the pollutants.

One feed system for this combustor is the underfeed stoker in which the fuel is fed by a worm feeder into the bottom of a retort. The fuel rises vertically in the retort and air enters through tuyeres in the sides. The fire is ignited at the top, and the flame front moves downward, and its speed is matched by the rising flow of coal, fulfilling the requirement of the flame front traveling in the opposite direction of the primary air. Volatile matter from the coal mixes with the air and ignites as it passes through the incandescent top layer of the bed thereby effectively controlling smoke emission.

Another feed system is the chain-grate stoker in which the fuel is fed from hoppers by gravity to a grate which consists of an endless chain extending into the boiler. The horizontal movement of the grate carries the fuel into the combustion chamber; the coal is carried forward as a thin layer on the top surface of the grate while air is delivered beneath it. As the fuel enters the combustion chamber, the top surface is ignited by radiation from a hot refractory arch, and the flame front then travels down through the coal bed, while the air comes up through it. At the end of the grate, the fuel has been burned and any residual ash is dropped into a container as the grate turns for the return journey.

See also: Combustion.

Downdraft Gasifier

By the conventional downdraft gasifier (co-current gasifier), biomass is fed at the top of the reactor and air intake is at the top or from the sides.

The gas leaves at the bottom of the reactor, so the fuel and the gas move in the same direction. The pyrolysis gasses are led through the oxidation zone (with high temperatures) and are more or less burnt or cracked. Therefore, the producer gas has low tar content and is suitable for engine applications. In practice, however, a tar-free gas is seldom if ever achieved over the whole operating range of the equipment. Because of the lower level of organic components in the condensate, downdraft gasifiers suffer less from environmental objections than updraft gasifiers.

The co-current fixed bed (down draft) gasifier is similar to the counter-current type, but the gasification agent gas flows in co-current configuration with the fuel (downwards, hence the name down draft gasifier). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting in energy efficiency on level with the counter-current type. Since all tars must pass through a hot bed of char in this configuration, tar levels are much lower than the counter-current type.

The drawbacks of the downdraft gasifier are (i) the high amounts of ash and dust particles in the gas, (ii) the inability to operate on a number of unprocessed fuels; often, pelletization or briquetting of the biomass is necessary, (iii) the outlet gas has a high temperature leading to a lower gasification efficiency, and (iv) the moisture content of the biomass must be less than 25 %.

See: Gasifiers, Gasification.

Downflow Fixed Bed Reactor

This reactor design commonly used in hydrodesulfurization of distillates is the fixed-bed reactor design in which the feedstock enters at the top of the reactor and the product leaves at the bottom of the reactor.

The catalyst remains in a stationary position (fixed-bed) with hydrogen and crude oil feedstock passing in a downflow direction through the catalyst bed. The hydrodesulfurization reaction is exothermic, and the temperature rises from the inlet to the outlet of each catalyst bed. With a high hydrogen consumption and subsequent large temperature rise, the reaction mixture can be quenched with cold recycled gas at intermediate points in the reactor system. This is achieved by dividing the catalyst charge into a series of catalyst beds, and the effluent from each catalyst bed is quenched to the inlet temperature of the next catalyst bed.

The extent of desulfurization is controlled by raising the inlet temperature to each catalyst bed to maintain constant catalyst activity over the course of the process. Fixed-bed reactors are mathematically modeled as plug-flow reactors with little back mixing in the catalyst beds. The first catalyst bed is poisoned with vanadium and nickel at the inlet to the bed and may be a cheaper catalyst (*guard bed*). As the catalyst is poisoned in the front of the bed, the temperature exothermic moves down the bed and the activity of the entire catalyst charge declines, thus requiring a raise in the reactor temperature over the course of the process sequence.

After catalyst regeneration, the reactors are opened and inspected, and the high metal content catalyst layer at the inlet to the first bed may be discarded and replaced with fresh catalyst. The catalyst loses activity after a series of

regenerations and, consequently, after a series of regenerations, it is necessary to replace the complete catalyst charge. In the case of high metal content feedstocks (such as residua), it is often necessary to replace the entire catalyst charge rather than to regenerate it. This is due to the fact that the metal contaminants cannot be removed by economical means during rapid regeneration and the metals have been reported to interfere with the combustion of carbon and sulfur, catalyzing the conversion of sulfur dioxide (SO_2) to sulfate (SO_4^{2-}) that has a permanent poisoning effect on the catalyst.

Fixed-bed hydrosulfurization units are generally used for distillate hydrosulfurization and may also be used for residuum hydrosulfurization but require special precautions in processing. The residuum must undergo two-stage electrostatic desalting so that salt deposits do not plug the inlet to the first catalyst bed, and the residuum must be low in vanadium and nickel content to avoid plugging the beds with metal deposits, hence the need for a guard bed in residuum hydrosulfurization reactors.

During the operation of a fixed-bed reactor, contaminants entering with fresh feed are filtered out and fill the voids between catalyst particles in the bed. The buildup of contaminants in the bed can result in the channeling of reactants through the bed and reducing the hydrosulfurization efficiency. As the flow pattern becomes distorted or restricted, the pressure drop throughout the catalyst bed increases. If the pressure drop becomes high enough, physical damage to the reactor internals can result. When high-pressure drops are observed throughout any portion of the reactor, the unit is shut down and the catalyst bed is skimmed and refilled.

With fixed-bed reactors, a balance must be reached between reaction rate and pressure drop across the catalyst bed. As catalyst particle size is decreased, the desulfurization reaction rate increases but so does the pressure drop across the catalyst bed. Expanded-bed reactors do not have this limitation, and small 1/32 inch (0.8 mm) extrudate catalysts or fine catalysts may be used without increasing the pressure drop.

See also: Descending Bed Reactor.

Drizo Process

The Drizo process is a glycol dehydration process in which the glycol is regenerated by solvent stripping instead of the conventional gas stripping. Solvent stripping allows much higher glycol purities than gas stripping (up to 99.99% w/w instead of the typical 99.95 wt%) and consequently allows to get much larger water dew point depressions: up to 100°C (180°F) and even higher in some cases. The solvent required by the Drizo process is usually an aromatic (BTEx-type) solvent, and in most cases, the process will even produce some liquid hydrocarbon derivatives.

The glycol dehydration option is an example of a process that provides absorption dehydration, and in the process, a liquid desiccant provides the means to absorb water from the gas stream. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) was, initially, the principal chemical agent in this process, has a strong affinity for water, and when the glycol is in contact with a stream of water-wet natural gas, the ethylene glycol absorbs the water from the gas stream. Initially, the process used ethylene glycol as the absorbent, but, with the advancement of the technology, glycol dehydration now involves the use of an aqueous solution of a glycol derivative in which the glycol is either diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the water-wet gas stream in a contactor.

The glycol solution will absorb water from the wet gas, and once absorbed, the glycol sinks to the bottom of the contactor while the natural gas, stripped of most of the water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through specialized equipment that is designed to vaporize only the water out of the solution where the boiling point differential facilitates removal of the water which makes it relatively easy to remove water from the glycol solution after which the glycol is recycled to the contactor.

The process regenerates the glycol by solvent stripping instead of the conventional gas stripping. Solvent stripping allows to obtain much higher glycol purities than gas stripping (up to 99.998 wt% instead of the typical 99.95 wt%) and consequently allows to get much larger water dew point depressions: up to 100°C (180 Glycol solvent stripping by condensates (instead of conventional gas stripping) allows (i) higher glycol purities down to < 1 ppmv water in treated gas, and (ii) reduced carbon dioxide emissions. The solvent required by the Drizo process is usually obtained from the BTEx present in many gas streams itself, and in most cases, the process will even produce some liquid hydrocarbons.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Drop Tube Furnace

A drop tube furnace (vertical tube furnace) is used for devolatilization and char combustion tests. The sample of the feedstock is injected into a hot (up to 1,500°C, 2,730°F) downward gas stream under laminar flow conditions for residence times up to 500 milliseconds. A gas mixing facility allows use of oxidizing or reducing atmosphere.

It is important to predict the combustion behavior of solid fuels such as biomass and biochar before their use in industrial equipment. The drop tube furnace can also be used to determine the events during the pyrolysis of biomass (for example, sawdust and pinewood, 120 to 250 μm size) at temperatures of up to 1,450°C (2,640°F) in both carbon dioxide and nitrogen atmospheres.

Typically, the furnace is electrically heated and is able to work at a maximum temperature of 1,300°C (2,375°F). The combustion chamber is a cylindrical ceramic tube with an inner diameter of 35 mm and a length of 1.75 m. The furnace wall temperatures are continuously monitored by thermocouples distributed along the combustion chamber. A water-cooled injector, placed at the top end of the drop tube furnace, is used to feed the pulverized grape pomace and the air to the combustion chamber. A twin-screw volumetric feeder transfers the pulverized-coal to an ejector system from which the particles are air-transported to the injector. The transport and secondary air are supplied by an air compressor (150 psi), with the flow rates being measured using mass flow controllers.

Dry-Ash-Free Basis

Dry-ash-free basis (daf basis) refers to the data from analysis calculated as if moisture and ash were removed.

The final results of the proximate analysis of carbonaceous materials are usually reported to the first decimal place; any subsequent figures have little or no significance. The final report of the analysis should always contain the results on a basis of air-dried fuel (i.e., the feedstock in its most stable condition and in which it was analyzed), but for purposes of classification or comparison, it is often necessary to convert to another basis such as dry feedstock, dry-ash-free feedstock, or as received feedstock. This allows comparison of the data on a basis that is not influenced by water or mineral matter content.

The analyses of a feedstock may be reported on different bases with regard to moisture and ash content. Thus, results that are *as determined* refer to the moisture condition of the sample during analyses in the laboratory; a frequent practice is to air-dry the sample, thereby bringing the moisture content to approximate equilibrium with the laboratory atmosphere in order to minimize gain or loss during sampling operations. Loss of weight during air-drying is determined to enable calculation on an *as-received* basis (the moisture condition when the sample arrived in the laboratory). This is, of course, equivalent to the *as-sampled* basis if no gain or loss of moisture occurs during the transportation to the laboratory from the sampling site. Attempts to retain the moisture at the *as-sampled* level include shipping in sealed containers with sealed plastic liners or in sealed plastic bags.

Analyses reported on a *dry* basis are calculated on the basis that there is no moisture associated with the sample. The moisture value is used for converting the *as determined* data to the *dry* basis. Analytical data that are reported on a *dry, ash-free* basis are calculated on assumption that there is no moisture or mineral matter associated with the sample. The values obtained for moisture determination and ash determination are used for the conversion.

The mineral matter in a feedstock loses weight during thermal conversion to ash because of the loss of water of constitution of clays, and the loss of carbon dioxide from carbonate minerals such as calcite. In addition, any chlorine in the feedstock is converted to hydrogen chloride but the change in weight may not be significant. Analyses and calorific values are determined on a mineral matter-free basis and the data presented with corrections for the mineral matter.

See also Proximate Analysis.

Dry Deposition

Dry deposition refers to the removal of both particles and gases as they come into contact with the land surface. The process is efficient as only a few gases (most notably carbon dioxide) show signs of global increase in spite of

the large emission of pollutants from both natural and anthropogenic sources. There are two types of deposition mechanisms: (i) dry deposition, which is the uptake at the surface of the Earth in the soil, a water system, or in vegetation, and (ii) wet deposition, which is formation of droplets followed by droplet precipitation (such as by rain) or impaction on the surface of the Earth (as, for example, fog droplets).

Also, often included in the category of dry deposition is the phenomenon known as gravitational sedimentation which occurs during periods without precipitation. These particles include (i) aerosols, (ii) sea salts, (iii) particulate matter, and (iv) adsorbed/reacted gases captured by vegetation. Related to this is the impaction is the capture of particles moving horizontally in the airstream by the vegetation canopy which (as a filtering effect) may accumulate large quantities of nutrients in some environments. On the other hand, wet deposition is the removal of pollution plume components by the action of rain. The wet deposition of radionuclides in a pollution plume by rain often forms so-called *hot spots* of radioactivity on the underlying surface.

Drying

At some stage of the production of any gaseous, liquid, and solid fuels, the feedstock and the products will, of necessity, need to be dried (i.e., the water will have to be removed).

Drying of the biomass fuel is advisable if fresh wet materials (moisture content 50-60% on wet basis) are to be gasified. Lowering the moisture content of the feedstock is associated with a better performance of the gasifier. Utilizing the exhaust gases from an internal combustion engine is a very efficient way to do so. The sensible heat in engine exhaust is sufficient to dry biomass from 70% down to 10%. Rotary kilns are the most applied dryers. The energy costs of drying are high, but these can be outweighed by the lower downstream gas cleaning requirements for dried feed.

In combustion systems, any water content in the fuel must be driven off before the first stage of combustion can occur, requiring energy, and thus reducing overall system efficiency and potentially reducing combustion temperature below the optimum. Reduction in combustion temperature below the optimum may result in incomplete combustion of the fuel giving rise to the emission of tars and creosote which may condense in the flue, especially if it is long or includes changes of direction, and particulates. The water may also condense in the flue, and all these may lead to corrosion of the flue and the gradual accretion of material leading to the potential for eventual blockages or fire.

Dryers can be broadly divided into two categories based on how heat is provided for drying. In direct dryers, the material gets heat from direct contact with a fluid providing the heat—either hot air or hot steam. With indirect drying, the material being dried is separated from the heat source by a heat exchange surface. One important consequence of indirect drying is that it is possible to recover the latent heat of evaporated water because the water vapor is not diluted by air. This can be done by drawing a vacuum on the material as it is drying and condensing the water vapor before a vacuum pump, or if the dryer is operated at a sufficiently high temperature, the water evaporates at an elevated pressure.

Directly heated dryers can be further divided into two more categories: air and superheated steam dryers (SSDs). In air dryers, hot air is contacted with the material to be dried. The air loses its sensible heat and provides the latent heat of evaporation to dry the material. The air also removes the water vapor that is evaporated. The material can be agitated by some mechanical means or by the flowing air.

In superheated steam dryers, the heating fluid is steam rather than air, but the concept is the same. The superheated steam is contacted with the biomass material and loses some of its sensible heat to provide the latent heat of evaporation to dry the fuel. The steam, however, remains above its saturation temperature, so it does not condense. The water vapor leaving the biomass is heated by the superheated steam, so the net result is a larger amount of steam at a lower temperature than when the steam entered the dryer. The excess steam is removed, and the remainder is reheated and recycled back to the dryer.

In the case of the indirectly heated dryer operated under a vacuum, or with a superheated steam dryer, the latent heat of evaporation of the water vapor is easy to recover because it is not diluted by air. With vacuum drying, this

heat is available only at a low temperature, but with superheated steam drying, the dryer can be designed to produce steam at practically any pressure for use in other parts of the plant.

There are several steps to drying – first, the material must be heated from the temperature at which it entered the dryer, up to the wet bulb temperature, to produce a driving force for water to leave the wet material. Next, any surface moisture on the material is evaporated—this occurs fairly quickly. Once all the surface moisture is removed, the material must be heated to drive water from the inside of the biomass to the surface so it can evaporate. This occurs during the falling rate period when the rate of drying drops as the material becomes drier. During the falling rate period, the surface temperature of the material remains close to the wet bulb temperature. Once the material is completely dry, it begins to heat up to the surrounding temperature, because water is no longer present to keep its temperature low.

There are two points in the drying process when there is a significant fire risk. The first occurs after the surface moisture has evaporated, but before an appreciable amount of water has been driven out from inside the biomass. During this very brief period, there is no water vapor near the surface to keep the fuel particle cool, and the surface can quickly heat up while the inside remains cool. If the surface remains hot for a long enough time, the material can ignite even if it is not completely dry. However, once the inside of the particle starts to drive water to the surface, a constant supply of moisture moving to the surface will keep it cool until it is completely dry.

The other time when fire is a concern is when material is over-dried. If the material loses all its moisture, it will begin to warm and can ignite when it reaches its combustion temperature, or when any gases evolved reach their flash point. Since the drying rate drops as biomass material gets drier, most dryers are not designed to completely dry the material. Over-drying would be expected to occur only during upset conditions or when processing a material with better drying properties than what the dryer was designed to handle.

The drying equipment can be further characterized according to the bed types used in the drying process which are (i) static bed, (ii) moving bed, (iii) fluidized bed, (iv) dilute bed, and (v) parallel flow equipment.

A *static bed* is a dense bed of particles with the particles resting on each other at the settled bulk density, and there is no relative motion among the solid particles. This would be typically encountered in a tray dryer where the solids are contained in a tray over which the drying gas flows. A *moving bed* is a slightly expanded bed where the particles can flow over one another. The flow can be induced either by gravity or by mechanical agitation. A *fluidized bed* is in an expanded condition where the upward superficial velocity above the bed is not high enough to carry the particles out of the reactor. However, the higher velocity due to the presence of the solids inside the denser fluidized bed is sufficient to drag the particles upward and greatly expand the bed even though not high enough to carry the particles out of the containment vessel. A *dilute bed* is in a fully expanded condition where the solid particles are so far apart that they have no influence on each other. Usually, the gas velocity is above the terminal settling velocity of the particles and the particles are carried out of the vessel with the gas. In the *parallel flow* equipment, the parallel flow occurs when the gas flow is parallel to the surface of the solids bed. The solids bed is usually in a static condition, and the contacting is primarily at the interface between the solids and gas. A small amount of gas penetration into the voids among the particles at the surface can occur. Perpendicular flow occurs when the gas flow is perpendicular to the surface of the solids. The solids bed is again usually in the static condition, and the gas impinges on its surface. Circulation occurs when the gas penetrates the bed and flows through the interstices among the solids more or less freely around the individual particles which can occur with solids beds in either the static, moving, fluidized, or dilute condition. The flow of gas can be either *cocurrent* with the solids, *countercurrent* against the flow of the solids, or *cross-current* perpendicular to the flow of the solids.

See: Biomass, Biomass – Feedstocks.

Dry Point

The dry point is the temperature at which the last drop of a liquid fuel evaporates in a distillation test.

In the corrected thermometer reading that is observed at the instant the last drop of liquid (exclusive of any drops or film of liquid on the side of the flask or on the temperature sensor) evaporates from the lowest point in the

distillation flask. The end point (final boiling point), rather than the dry point, is intended for general use. The dry point can be reported in connection with special purpose naphtha, such as naphtha used in the paint industry. Also, it is substituted for the end point (final boiling point) whenever the sample is of such a nature that the precision of the end point (final boiling point) cannot consistently meet the necessary requirements.

Dry Sorption Processes

Dry sorption processes are employed to scavenge hydrogen sulfide and organic sulfur compounds (mercaptans) from gas streams through reactions with a solid-based media. They are typically non-regenerable, although some are partially regenerable, losing activity upon each regeneration cycle.

Most dry sorption processes are governed by the reaction of a metal oxide (such as iron oxide and zinc oxide) with hydrogen sulfide to form a metal sulfide compound. For regenerable reactions, the metal sulfide compound can then react with oxygen to produce elemental sulfur and a regenerated metal oxide.

Dry sorption processes can be categorized into two subgroups which are (i) oxidation to sulfur and (ii) oxidation to oxides of sulfur. Since these processes rely on oxidation, gas constituents that cannot be oxidized under the process conditions will not be removed. This is advantageous when dealing with a gas stream where only hydrogen sulfide and, in some cases, carbon dioxide are required to be removed with minimal loss losses of methane due to adsorption. The main product of sulfur oxidation to oxides of sulfur is sulfur dioxide which because this is a controlled exhaust gas, poses a threat to equipment, due to corrosion and poisoning of fuel cell membranes and requires additional gas processing to achieve air discharge standards.

See also: Adsorption.

Dust Collectors

In the biomass-to-fuels industry, the raw biomass typically undergoes a number of crushing, grinding, cleaning, drying, and product sizing operations before (and after) it is converted into a marketable commodity. These operations are highly mechanized, and both individually and collectively, these processes can generate large amounts of dust (particulate matter). If control technologies are inadequate, hazardous levels of respirable dust may be liberated into the work environment, potentially exposing workers. Accordingly, in many countries, regulations are in place to limit the respirable dust exposure of workers. Engineering controls are implemented in many industrial operations in an effort to reduce dust generation and limit worker exposure.

Depending on the size, these particles can become hazardous to worker health, particularly when suspended in air. The largest size particle that can be suspended in air for long periods of time from wind velocity acting upon it is on the order of 60 microns (micrometers, μm). Particles ranging from approximately 60 to 2,000 μm can also become suspended in air, but they only reach heights up to approximately three feet above the ground before they fall back to the surface. Particles larger than approximately 2,000 μm generally creep or roll along the surface due to wind velocity acting upon them. These larger particles of dust can affect the nasal passages, causing an irritated and congested nose, and might also cause an irritant cough should they deposit in the throat. Smaller airborne particles of dust, which can remain suspended in air for hours, pose a greater risk to the respiratory system when inhaled. In general, the smaller the aerodynamic diameter of the inhaled dust particle, the more likely it will be deposited more deeply in the respiratory tract.

Thus, dust collectors (or, for that matter, any type of particulate matter collectors) are used in many processes to either recover valuable granular solid or powder from process streams or to remove granular solid pollutants from exhaust gases prior to venting to the atmosphere. Dust collection is an online process for collecting any process-generated dust from the source point on a continuous basis, and these collectors may be of single unit construction, or a collection of devices used to separate particulate matter from the process air. They are often used as an air pollution control device to maintain or improve air quality. Mist collectors remove particulate matter in the form of fine liquid droplets from the air. They are often used for the collection of metal working fluids, and coolant or oil mists. Mist collectors are often used to improve or maintain the quality of air in the workplace environment. Fume and smoke

collectors are used to remove submicrometer size particulate from the air. They effectively reduce or eliminate particulate matter and gas streams from many industrial processes such as welding, rubber and plastic processing, high speed machining with coolants, tempering, and quenching.

Dust collectors vary widely in design, operation, effectiveness, space requirements, construction, and capital, operating, and maintenance costs but can be generally separated into five common types: (i) an ambient unit, which is a free-hanging system for use when applications limit the use of source-capture arms or ductwork, (ii) a collection booth, which allows the worker greater freedom of movement. they are often portable, (iii) downdraft tables, which form a self-contained portable filtration system that removes harmful particulates and returns filtered air back into the facility with no external ventilation required, (iv) a source collector or portable units which are used for collecting dust, mist, fumes, or smoke at the source, and (v) stationary units – an example of a stationary collector is a baghouse.

More specifically, there are five principal types of industrial dust collectors which are (i) inertial separators, (ii) fabric filters, (iii) wet scrubbers, (iv) electrostatic precipitators, and (v) unit collectors. Thus, systems for fines removal may only contain a single filtration system (such as a filter bag or cartridge). However, most units utilize a primary and secondary separation/filtration system. Furthermore, some units may have third and fourth stage filtration. All separation and filtration systems used within the unit should be specified.

Important parameters in specifying dust collectors include airflow, the velocity of the air stream created by the vacuum producer; system power, the power of the system motor, usually specified in horsepower; storage capacity for dust and particles; and minimum particle size filtered by the unit.

Dust Control

The presence of dust can cause serious problems in many dry cleaning plants and in the pretreatment sections of wet cleaning plants. In addition, dust containment is an integral part of all thermal drying units. The need for dust collection arises because of air pollution control, safety- and health-hazard elimination, and reduction of equipment maintenance costs. In addition to the economic and hazards, coal dust can present serious explosion hazards. Certain bituminous coals and anthracites also continue to release measurable quantities of methane gas for days, and sometimes weeks, after they have been mined, which increases the possibility of explosion. Provision of efficient ventilation and restriction of electrical or thermal sources of ignition are required by regulation.

The main sources of dust emissions are crushers, breakers, dust removers, dry screens, and transfer points between the units in coal pretreatment operations. The size of the coal particles that become airborne generally falls into the range 1 to 100 microns ($1\text{--}100 \times 10^{-6}$ meters), and particles larger than this usually deposit close to the point of origin. It is the usual practice to extract the dust clouds from the various sources through ducts that exhaust to a central air-cleaning unit, although some equipment may include integral dust suppression devices.

Dust collection equipment used at cleaning plants includes (i) dry units such as cyclones, dynamic collectors, and baghouses – also known as fabric filters – and (ii) wet units such as dynamic, impingement, or centrifugal devices, or gravity, disintegrator, or venturi scrubber systems. Other sources of dust are windblown losses from storage piles and from railcars during loading and transportation. Various chemical treatments are available for stockpile sealing and are being used for spraying the tops of railcars; active stockpiles present an almost insurmountable problem.

Dustiness Index

The dustiness index is a means of determining the relative values that represent the amount of dust produced when coal is handled in a standard manner. Dust removal is an important aspect of safety, and there have been constant attempts to improve dust removal technology. As the techniques have been developed, the predictability of how coal will behave, in terms of the dust produced, under certain conditions has also been sought.

To determine the dustiness index, a large sample is placed on a slide plate in a metal cabinet of prescribed size. When the plate is withdrawn, the sample falls into a drawer and, after five seconds, two slides are inserted into the box. The slides collect suspended dust particles for two minutes (coarse dust) or for ten minutes (fine dust).

The dustiness index is reported as forty times the gram weight of dust that has settled after either two minutes or after an additional eight minutes.

See also: Dust, Dust Collectors, Dust Control.

Dutch Oven Furnace

A Dutch oven furnace is one of the earliest types of furnaces, having a large, rectangular box lined with firebrick (refractory) on the sides and top, commonly used for burning wood.

Various boiler firing configurations are used for burning wood waste. One common type of boiler used in smaller operations is the Dutch oven. This unit is widely used because it can burn fuels with high moisture content. Fuel is fed into the oven through an opening in the top of a refractory-lined furnace. The fuel accumulates in a cone-shaped pile on a flat or sloping grate. Combustion is accomplished in two stages: (i) drying and gasification, which occurs in the primary furnace, which is separated from the secondary furnace chamber by a bridge wall, and (ii) combustion of the gaseous products in which the combustion is completed in the secondary chamber before gases enter the boiler section. The large mass of refractory helps to stabilize combustion rates but also causes a slow response to fluctuating steam demand. The furnace was commonly used for burning wood. Heat is stored in the refractory lining (firebrick) and radiated to a conical fuel pile in the center of the furnace.

Another type of furnace is the fuel cell oven, in which the fuel is dropped onto suspended fixed grates and is fired in a pile. Unlike the Dutch oven, the refractory-lined fuel cell also uses combustion air preheating and positioning of secondary and tertiary air injection ports to improve boiler efficiency. Because of the overall design and operating similarities, however, the Dutch oven boilers and fuel cell oven boilers have comparable emission characteristics.

See: Combustion.

E85

E85 is an alcohol fuel mixture containing 85% ethanol and 15% gasoline by volume. E85 has an octane rating higher than that of typical rating for regular gasoline of 87, or the rating for premium gasoline of 91 to 94 (Table E-1). This allows it to be used in higher compression engines which tend to produce more power per unit of displacement than their gasoline counterparts.

Table E-1 Examples of the selected properties of E85 and crude oil-based gasoline.

Category	E85	Gasoline
Formula	$\text{CH}_3\text{CH}_2\text{OH}$	C_4 to C_8 (approximately)
Octane number	100	85 to 94
Source	renewable	crude oil
Energy content*	80,000	109,000 to 125,000

*Btu per gallon

The octane number is often derived by using the blending octane value of octane in gasoline. More correctly, the actual octane value of ethanol is 94 to 96 when it is calculated using the research octane number (R) and the motor octane number (M), thus:

$$\text{Octane value} = (\text{R} + \text{M}) / 2.$$

E85 has an octane rating higher than that of regular gasoline's typical rating of 87, or 91 to 93 for premium gasoline. This allows it to be used in higher compression engines which tend to produce more power per unit of displacement than their gasoline counterparts. One complication is that use of gasoline in an engine with a high enough compression ratio to use E85 efficiently would likely result in catastrophic failure due to engine detonation, as the octane rating of gasoline is not high enough to withstand the greater compression ratios in use in an engine specifically designed to run on E85. Use of E85 in an engine designed specifically for gasoline would result in a loss of the potential efficiency that it is possible to gain with this fuel. Using E85 in a gasoline engine has the drawback of achieving lower fuel economy as more fuel is needed per unit air (stoichiometric fuel ratio) to run the engine in comparison with gasoline. This corresponds to a lower heating value (units of energy per unit mass) for E85 than gasoline.

See also: Biofuel, Gasohol, Gasoline, Octane Number.

Earth System

The Earth system consists of three main systems (often referred to as spheres) – (i) the atmosphere, which is the gases that surround the Earth, (ii) the aquasphere, which encompasses the water systems of the Earth, and (iii) the geosphere, which is the land systems of the Earth.

The first system, the atmosphere, is an envelope of gas that keeps the planet warm and provides oxygen for breathing and carbon dioxide for photosynthesis. The second system comprises the areas of Earth that are covered with amounts of water, called the aquasphere, and the sub-system, often referred to as the hydrosphere which excludes that part of the aquasphere that contains large quantities of ice at the poles and elsewhere is referred to as the cryosphere.

Then, there is the geosphere which consists of the interior and the surface of Earth, both of which are made up of rocks. The limited part of the planet that can support living flora and fauna comprises part of the geosphere that may also be referred to as the biosphere. Furthermore, the three systems (the aquasphere, the atmosphere, and the geosphere) and the various sub-systems (the hydrosphere, the cryosphere, and the biosphere) are complex systems that interact to maintain the Earth system as it currently exists.

Ebullated Bed Reactor

Ebullating bed technologies were first introduced in the 1960s in an attempt to overcome problems of catalyst ageing and mal-distribution in fixed bed designs. In this approach, hydrogen and feed enter at the bottom of the reactor, thereby expanding the catalyst bed. Although catalyst performance can be kept constant because catalyst can be replaced on line, the ebullated bed results in a back mixed reactor so desulfurization and hydroconversion are less than obtainable in a fixed-bed unit. In some respects, an ebullating bed reactor is a reactor similar to a fluidized bed but operated at higher gas velocities, such that a portion of the solids is carried out with the up-flowing gas.

An ebullated bed reactor (slurry bed reactor) is a type of fluidized bed in which catalyst particles are held in suspension by the upward movement of the liquid reactant and gas flow.

Ebullated bed units, unlike any other hydrotreaters, use a fluidized bed of hydroprocessing catalyst with continuous addition and removal of catalyst to maintain system activity. In ebullated bed reactors, hydrogen-rich recycle gas bubbles up through a mixture of oil and catalyst particles to provide three-phase turbulent mixing. The reaction environment can be nearly isothermal, which improves product selectivity. At the top of the reactor, catalyst particles are disengaged from the process fluids, which are separated in downstream flash drums. Most of the catalyst goes back to the reactor. Some is withdrawn and replaced with fresh catalyst.

Unlike fixed bed residuum catalyst systems, which can use many different catalysts to accomplish specific objectives, ebullated bed units typically use only one catalyst per reactor. That single catalyst must balance the unit requirements for demetallation (demetallization), desulfurization, and conversion.

Depending on the feedstock and the process needs, the ebullated bed can be staged in one or more initial reactors of a series, the product being fed to a subsequent ebullated or fixed bed reactor, or reactors. If desired, an ebullating bed from which aged catalyst is stratified and removed, while fresh or regenerated catalyst is added to the top of the bed, can also constitute the final reactor, or reactors, of the series. The ebullating bed reactor can be employed in series or in parallel.

See also: Ebullated Bed.

Control of sediment formation is the biggest issue in most ebullated bed resid units. When the unit is operated for high conversion, sediment formation increases, which causes problems in downstream equipment and eventual shutdown for cleaning. Albemarle has developed catalysts specifically designed to achieve high conversion activity while controlling sediment at a level which ensure long operating cycles.

The ebullated-bed reactor system overcomes problems encountered with fixed-bed reactors when processing difficult feedstocks (such as heavy crude oil, extra heavy crude oil, and tar sand bitumen) or when high processing severity is required. The bed of extrudate catalyst is fluidized (ebullated) by the lift of hydrogen and feed oil and recycled reactor liquid. The ebullated catalyst is well mixed and can be added and withdrawn from the reactor while at operating conditions.

See also: Fixed Bed Reactor.

Ecological Cycles

The ecological cycles are the various self-regulating processes that recycle the limited resources of the Earth (water, carbon, nitrogen, and other elements) that are essential to sustain life. Understanding how local cycles fit into global cycles is essential to make the best possible management decisions to maintain ecosystem health and productivity for now and the future.

There are biogeochemical cycles for the chemical elements (such as calcium, carbon, hydrogen, mercury, nitrogen, oxygen, phosphorus, selenium, and sulfur) as well as cycles for water and silica; macroscopic cycles such as the rock cycle as well as human-induced cycles for synthetic compounds such as polychlorinated biphenyl derivatives (PCBs). In some cycles, there are *reservoirs* where a substance remains for a long period of time.

There are several ecological cycles that also need a clearer and more detailed definition as each cycle plays an important role in the interrelationship of the various ecological systems to the environment as a whole. These cycles can be perturbed by anthropogenic stress as well as by natural occurrences. For example, the oxygen cycle illustrates the role of oxygen in the land water and air, either as oxygen per se or combined with carbon as carbon dioxide and as mineral carbonate derivatives. The cycle also includes industrial activities (such as fossil fuel burning) and natural activities (represented by volcanic activity). The nitrogen cycle relates not only to nitrogen in the atmosphere but also to nitrogen fixation in the soil and its use in plant growth.

The water cycle (also referred to as the hydrologic cycle) is the means by which water is transported throughout several ecosystems. In theory, there should be a harmonious balance between the water movement on the earth. Indeed, there should be a harmonious balance between the atmosphere, the water systems, and the land systems. But the existence of contrasting desert areas and tropical rain forests speaks to the apparent imbalance in these cycles, particularly in the hydrological cycle. A subcategory of the hydrological cycle involves the dispersion of water in various groundwater systems. These systems are responsible for the availability of water to the various flora and fauna in a particular region. The water availability of water from groundwater systems is considered, perhaps, to be more important than water availability from lakes and rivers. However, the interrelationships of water in the whole hydrological cycle are the most important features of this cycle. For example, the biogeochemical cycle (also called the substance turnover or cycling of substances) is a pathway by which a chemical substance moves through biotic compartments the biosphere) and through abiotic compartments of the Earth (such as the atmosphere, the hydrosphere, and the lithosphere).

The Earth system contains several great cycles in which key materials are transported through the environment. In general, cycles occur in closed systems; at the global scale, many systems may be assumed to be closed because the Earth receives negligible quantities of minerals from space (as a result of meteorite impacts) and because only limited quantities of materials can escape the atmosphere of the Earth.

The biogeochemical cycles operate at the global scale and involve all of the main components of the Earth system in which materials are transferred continually between the atmosphere, the aquasphere, and the geosphere. However, since the biogeochemical cycles involve elements that are essential for life, organisms play a vital part in those cycles. Typically then, the biogeochemical cycles involve an inorganic component (the abiotic part of the cycle, including sedimentary and atmospheric phases) and an organic component (comprising plants and animals, both living and dead). Like other environmental systems, biogeochemical cycles involve the flow of substances between stores (also known as reservoirs) in the geosphere, atmosphere, hydrosphere, and biosphere. Water plays a vital role in mediating many of the flows between stores. Three of the key biogeochemical cycles are the nitrogen, carbon, and sulfur cycles.

The nitrogen cycle is a relatively fast and complex cycle. Most of the atmosphere consists of gaseous nitrogen which is fixed (in other words, made available for use by plants) biologically in soils. Soil bacteria convert nitrogen to ammonia; this, together with inorganic nitrate, is absorbed by plant roots and converted to organic compounds (such as proteins) in plant tissues. These compounds are eaten and consumed by herbivorous animal. In turn, nitrogenous compounds are passed to carnivores, and they are ultimately returned to the soil in the form of nitrogenous waste products (such as urine and fecal matter) and as a result of the death and decomposition of organisms. Bacteria then convert the organic nitrogen compounds into ammonia and ammonium compounds, which are then converted by bacteria into nitrites and then nitrates, which are then available for re-uptake by plants.

Some of the nitrogenous compounds that are not absorbed by plants are leached from the soil into groundwater, surface water, and ultimately into seas and oceans. Of that nitrogenous material, some is used by aquatic plants, some accumulates as organic sediment, and some evaporates into the atmosphere. The cycle is completed by denitrifying bacteria which eventually convert nitrates and nitrites to ammonia, nitrogen, and nitrogen oxides.

The carbon cycle is a cycle in which carbon is stored in the atmosphere in the form of carbon dioxide, which is absorbed by plants and converted to carbohydrates by the process of photosynthesis. The cycle then follows the food chain, with carbohydrates being consumed by herbivores and then carnivores, being metabolized during the process of respiration. Carbon dioxide is returned to the atmosphere as animals exhale and when organic waste and dead

organisms decay. Vegetation and animals are thus important stores of carbon, although that carbon may be rapidly returned to the atmosphere if vegetation is burned. Soils are also important reservoirs for carbon. Atmospheric carbon dioxide is soluble in water, in which it forms carbonic acid, which forms bicarbonate ions and carbonate ions, which in turn form salts (such as the insoluble calcium carbonate, which accumulates in marine sediments, marine organisms, and carbonate rocks, such as limestone). Carbon is typically stored in these forms until it is released to the atmosphere by chemical weathering.

The sulfur cycle is a cycle in which sulfur is released into the atmosphere during volcanic eruptions (in the forms of sulfurous gas, dust, and particles) and as a result of the weathering of rocks. The oceans also play an important role in the sulfur cycle, as marine phytoplankton produce dimethyl sulfide, some of which enters the atmosphere and is converted to sulfur dioxide and sulfate aerosols. These compounds are ultimately converted to sulfuric acid and are deposited on the surface of the Earth as part of the precipitation. In terrestrial ecosystems, bacteria break down sulfurous compounds and release the sulfur to the atmosphere again, mainly in the form of hydrogen sulfide.

Finally, it must be noted that the biogeochemical cycles have been modified substantially by human activities which is necessary for consideration to understand the various environmental issues related to human activities.

See also: Biogeochemical Cycles.

Ecosystem

An ecosystem is a community of living organisms (biotic components) that exists in conjunction with the non-living (abiotic) components of the environment. These biotic and abiotic components are linked together through nutrient cycles, and energy flows such as when energy enters the system and is incorporated into the plant tissues through the photosynthetic process. By feeding on plants (the flora) and on one another, animals (the fauna) play an important role in the movement of matter and energy through the system. This process also influences the quantity of plant biomass and microbial biomass present in the ecosystem.

Thus, an ecosystem works as a unit in an efficient and organized way and receives energy that is passed on through the components of the ecosystem, and, in fact, all life depends on this flow of energy. Green plants (including phytoplankton species) are able to trap the solar energy in an ecosystem, and they make use of this energy for their growth and maintenance. Heterotrophic species (or consumers) obtain the energy requirements from this stored energy (in green plants) as food and use it for their development, growth, maintenance, or other life activities. All life forms in an ecosystem are linked together by the flow of energy. Besides energy, various nutrients and water, which are also required for life processes, are exchanged by the biotic components within themselves and with the abiotic components.

Soil is a critical part of an ecosystem. It provides important nutrients for the plants. It helps anchor the plants to keep them in place. Soil absorbs and holds water for plants and animals to use and provides a home for lots of living organisms. The atmosphere provides oxygen and carbon dioxide for the plants and animals in an ecosystem. The atmosphere is also part of the water cycle. Without the complex interactions and elements in the atmosphere, there would be no life on Earth. The heat and light from the Sun are critical parts of an ecosystem. The heat from the Sun helps water evaporate and return to the atmosphere where it is cycled back into water. The heat also keeps plants and animals warm. The light from the Sun is necessary for photosynthesis, so that plants have the energy they need to make food. Without water, there would be no life. Water is a large percentage of the cells that make up all living organisms. Water is also used by plants to carry and distribute the nutrients they need to survive.

Examples of ecosystems are (i) an agroecosystem, (ii) an aquatic ecosystem, (iii) a coral reef, (iv) a desert, (v) a forest, (vi) a human ecosystem, (vii) a littoral zone, also known as the nearshore which is the part of a sea, lake, or river that is close to the shore, (viii) a marine ecosystem, (ix) prairie, (x) rainforest, (xi) a savanna, (xii) a steppe, (xiii) a taiga, which is the conifer forest that lies between the broad-leaved forest and the tundra, (xiv) a tundra, and (xv) an urban ecosystem. Biomes are globally similar areas, including ecosystems, as regards combinations of plants, animals, soil organisms, and climatic conditions. They have certain common factors, such as plant structures (trees, shrubs, and grasses), leaf types (broadleaf, needles), plant spacing (forest, woodland, savanna), and climate. The basic types of biomes are (i) land, (ii) freshwater, and (iii) marine biomes.

Resource inputs to an ecosystem are generally controlled by external processes such as climate and the parent material in the system, and resource availability within the ecosystem is controlled by internal factors such as decomposition and root competition. Anthropogenic influences also influence the ecosystem.

See also: Earth System, Ecological Cycles.

E-Gas Process

The E-Gas process features a two-stage gasifier design in which the gasifier is refractory-lined and uses coal-water slurry feed. The two-stage gasifier is a coal-water slurry fed, oxygen-blown, refractory-lined gasifier with continuous slag removal system and dry particulate removal. The process is suitable for a wide range of feedstocks.

The first stage of the gasifier has two opposed, horizontally-oriented feed injectors. The synthesis gas exits the top of the first stage, and slag flows out of the bottom into a water bath. The synthesis gas produced by the first stage enters the second stage at temperatures comparable to the exit temperatures of the other two entrained flow gasifiers. Additional coal-water slurry is injected into this hot syngas in the second gasifier stage, but no additional oxygen is injected. Endothermic gasification reactions occur between the hot syngas and the second-stage coal feed. This lowers the temperature of the syngas and increases the cold gas efficiency of the process. Upon exiting the top of the second stage of the gasifier, the syngas passes through a syngas cooler which features a firetube design. The cooled syngas then enters a rigid barrier filter where any unconverted char from the second stage is collected and recycled back to the first stage of the gasifier where the hotter temperatures ensure near complete carbon conversion.

See also: Two-Stage Gasification.

Electrical Energy

Electrical energy is a form of energy resulting from the flow of an electric charge, typically through a wire. Energy is the ability to do work or apply force to move an object which is caused by the movement of charged particles through a wire or other medium called current or electricity.

Electrical energy can be used produce magnetic fields, which can be used to propel motors. It is very transformable and can be used to produce other forms of radiant energy, such as radio waves, microwaves, radiant heat, and light.

The fundamental principle of electricity generation was discovered during the 1820s and early 1830s by Michael Faraday.

In the modern world, electricity is most often generated at a power station by electromechanical generators, primarily driven by heat engines fueled by chemical combustion or nuclear fission as well as by other means such as the kinetic energy of flowing water and wind. There are many other technologies that can be and are used to generate electricity such as solar photovoltaics and geothermal power.

See also: Electricity Generation, Geothermal Energy, Hydrokinetic Energy, Ocean Energy, Solar Power, Wind Energy.

Electricity Generation – Equipment

Electric generators were known in simple forms from the discovery of electromagnetic induction in the 1830s. In general, some form of prime mover such as an engine or the turbines described above, drives a rotating magnetic field past stationary coils of wire thereby turning mechanical energy into electricity.

Almost all commercial electrical power on Earth is generated with a turbine, driven by wind, water, steam, or burning gas. The turbine drives a generator, thus transforming its mechanical energy into electrical energy by electromagnetic induction. There are many different methods of developing mechanical energy, including heat engines, hydropower, wind power, and tidal power.

Turbine types include: (i) steam in which water is boiled by fuel combustion, (ii) nuclear fission heat created in a nuclear reactor creates steam, (iii) renewable energy in which the steam is generated by biomass combustion, solar thermal energy, or geothermal energy, (iv) water energy which is captured by a water turbine from the movement of water such as from falling water, the rise and fall of tides or ocean thermal currents, (v) the windmill which is a form of the wind turbine.

See also: Turbine.

Electricity Generation from Conventional Fuels

Electricity generation is the process of generating electric power from sources of primary energy, such as fossil fuels. Electricity must be produced from other forms of energy in power plants (also called power stations). Electricity is most often generated at power plants by electromagnetic generators, primarily driven by heat engines fueled by combustion or nuclear fission but also by other means such as the kinetic energy of flowing water and wind. Other energy sources include solar photovoltaics and geothermal power.

The production of electric power by the combustion of coal, crude oil, or natural gas is a mature and well-established technology in the industrialized countries of the world, although other options are available. Put simply, power plants produce electricity by burning coal in a boiler to produce steam which, under high pressure, flows into a turbine, which spins a generator to create electricity. The steam is then cooled, condensed back into water, and returned to the boiler to start the process over. Thus:

Feedstock → boiler → turbine → generator → electricity → user

In the process of using a carbonaceous feedstock to generate electricity, the chemical energy of the feedstock is converted to thermal energy and the heat is used to generate high pressure steam that passes through a turbine to generate electricity. In a combined cycle, the feedstock is first combusted in a combustion turbine, using the heated exhaust gases to generate electricity. After these exhaust gases are recovered, they heat water in a boiler, creating steam to drive a second turbine. Apart from combustion, fossil fuels can also be gasified producing synthesis gas (syngas) – mixtures of carbon monoxide (CO) and hydrogen (H₂) – which can be directly used as a fuel for power generation. Alternatively, the hydrogen can be separated and used as a fuel in an open or combined cycle process.

The advent of stricter environmental controls on effluents from power plants, especially with respect to sulfur oxides, has required that new types of combustion/pollution control technology are emerging. In fact, the increased utilization of coal in place of oil and gas for combustion applications in the United States is motivating near-term development and implementation of alternative technologies for electricity generation from coal.

See also: Turbine.

Electricity Generation from Crops

In recent years, biofuels have become more attractive to many countries as possible replacements for fossil fuels. Therefore, understanding the sustainability of this renewable resource is important. There are many benefits associated with the use of biofuels such as reduced greenhouse gas emissions, lower cost than fossil fuels, and renewability, etc. These energy crops can be used to generate electricity. Wood cellulose and biofuel in conjunction with stationary electricity generation have been shown to be very efficient.

The projected increase in use/need of energy crops begs the question of whether this resource is sustainable. Increased biofuel production draws on issues relating to changes in land use, impacts on ecosystem (soil and water resources), and adds to competition of land space for use to grow energy crops, food, or feed crops. Plants best suited for future bioenergy feedstocks should be fast growing, high yielding, and require little energy input for growth and harvest. The use of energy crops for energy production can be beneficial because of its carbon neutrality and represents a cheaper alternative to fossil fuels while being extremely diverse in the species of plants that can be used for energy production. But issues regarding cost (more expensive than other renewable energy sources), efficiency, and

space required to maintain production need to be considered and improved upon to allow for the use of biofuels to be commonly adopted.

See also: Energy Crops, Electricity Generation from Conventional Fuels.

Electricity Generation from Waste

Waste-to-energy (WtE) or energy-from-waste (EfW) is the process of generating energy in the form of electricity and/or heat from the primary treatment of waste.

Incineration, the combustion of organic material such as waste with energy recovery, is the most common WtE implementation. Modern incinerators reduce the volume of the original waste by 95-96%, depending upon composition and degree of recovery of materials such as metals from the ash for recycling.

The method of incineration to convert municipal solid waste (MSW) is a relatively old method of WtE generation. Incineration generally entails burning waste (residual MSW, commercial, industrial, and RDF) to boil water which powers steam generators that generate electric energy and heat to be used in homes, businesses, institutions, and industries. One problem associated is the potential for pollutants to enter the atmosphere with the flue gases from the boiler. These pollutants can be acidic and in the 1980s were reported to cause environmental degradation by turning rain into acid rain. Modern incinerators incorporate carefully engineered primary and secondary burn chambers, and controlled burners designed to burn completely with the lowest possible emissions, eliminating, in some cases, the need for lime scrubbers and electro-static precipitators on smokestacks.

By passing the smoke through the basic lime scrubbers, any acids that might be in the smoke are neutralized which prevents the acid from reaching the atmosphere and hurting the environment. Many other devices, such as fabric filters, reactors, and catalysts destroy or capture other regulated pollutants.

See also: Combustion, Gas Cleaning, Gas Processing, Gas Treating.

Electricity Generation from Wood

Electricity generation from woody biomass has been growing steadily since 1990 with an approximate 2 to 3% average annual growth. As the second largest renewable electricity source after hydropower, solid biomass accounted for more than 5% of renewable electricity generation. Of the electricity generated from solid biomass, more than 40 TWh is accounted for by the USA. The second largest producer of electricity from solid biomass is Finland (>8 TWh).

Other big producers are Japan and Canada; in fact, electricity is produced from solid biomass in most Organisation for Economic Co-operation and Development (OECD) member countries. This mainly involves the combustion of commercial woody fuels in modern devices, for example, woodchip-fired co-generation plants for heat and power. Other applications are industrial heat supply and co-firing with coal for large-scale power generation.

See also: Energy From Crops, Energy From Wood.

Electricity Generator

An electricity generator (electric generator) is a machine that converts mechanical energy to electrical energy. The mechanical energy can be supplied by the prime mover such as (i) a combustion engine, (ii) a steam engine, (iii) water falling through turbine, or (iv) any such mechanism that can be a source of mechanical energy. Usually, this energy is obtained from a rotating shaft (also called the armature of the generator). The electric energy then produced can be used for power transmission to commercial, industrial, or even domestic level.

An electric generator is a device that converts mechanical energy obtained from an external source into electrical energy as the output. However, the generator does not actually create the electrical energy but uses the mechanical energy supplied to it to force the movement of electric charges present in the wire of its windings through an external electric circuit. This flow of electric charges constitutes the output electric current supplied by the generator.

The modern-day generator works on the principle of electromagnetic induction discovered by Michael Faraday in 1831-1832 who found that the flow of electric charges could be induced by moving an electrical conductor, such as a wire that contains electric charges, in a magnetic field. This movement creates a voltage difference between the two ends of the wire or electrical conductor, which in turn causes the electric charges to flow, thus generating electric current.

Currently, there are five major types of electric generators, classified according to the manner in which their field flux is produced which are (i) the separately excited generator, in which the field flux is derived from a separate power source independent of the generator itself, (ii) the shunt generator, in which the field flux is derived by connecting the field circuit directly across the terminals of the generator, (iii) the series generator, in which the field flux is produced by connecting the field circuit in series with the armature of the generator, (iv) the commutatively compound generator, in which both a shunt and a series field are present and their efforts are additive, and (v) the differentially compound generator, in which a differentially compounded generator, both a shunt and a series field are present, but their efforts are subtracted.

Currently, three basic types of power plants generate most of the electricity in the United States and are fossil fuel power plants, nuclear power plants, and hydropower power plants. There are also wind, geothermal, waste-to-energy, and solar power plants.

Fossil fuel plants burn coal, natural gas, or crude oil which use the chemical energy in fossil fuels to superheat water into steam, which drives a steam generator. Fossil fuel plants are sometimes called thermal power plants because they use heat to generate electricity. Nuclear plants generate electricity much as fossil fuel plants do, except that the furnace is a reactor and the fuel is typically uranium. In a nuclear plant, a reactor splits uranium atoms into smaller elements, producing a great amount of heat in the process. The heat is used to superheat water into high-pressure steam, which drives a turbine generator. Like fossil fuel plants, nuclear power plants are thermal plants because they use heat to generate electricity. Hydropower plants use the gravitational force of falling water to generate electricity which is the cheapest way to produce electricity in the United States, but there are places where new dams can be built economically. There are many existing dams that could be retrofitted with turbines and generators.

See also: Turbine.

Electrochemical Processes

Electrochemical processes are widely used in the energy process industries, and the basic apparatus of an electrochemical process is the electrolytic cell which consists of an anode where oxidation reactions occur, a cathode where reduction reactions occur, an electrolyte which contains in ionic form the material to be converted, and a power supply to provide a direct current voltage between the electrodes. The cell may also contain one or more membranes between the electrodes which permit the passage of either cations or anions, but not both.

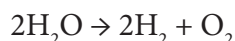
The processes are used frequently in the fuel industries for minimizing waste and converting toxic waste into more benign products as well as recycling process streams, nuclear decontamination, and wastewater treatment. Metals recovery can be achieved by electroplating the metal ions out of an aqueous waste stream since electrochemistry has the advantage that the metal can be recovered in its most valuable form – as the pure metal.

See also: Electrostatic Precipitator.

Electrolysis

Electrolysis is the process by which an electric current is passed through water and breaks the chemical bonds between hydrogen and oxygen. In the process, an electrolyte, a fluid chemical substance that can carry a current, aids in the bond-breaking procedure. Once the bonds are broken, the atomic components (hydrogen and oxygen) become either positive or negative ions (charged particles). Two terminals (anode and cathode) also have positive and negative charges, drawing the resulting ions toward them. Generally, the positive hydrogen ions gather at the anode (which is negative), while the negative oxygen ions reside at the cathode (which is positive). Gas is then formed at either terminal.

Water, being covalent, has very few ions in it, but the addition of a dilute acid or a salt such as sodium chloride provides sufficient ions to pass significant current. If sulfuric acid is used, as in the rechargeable battery of an automobile, the ions produced are H^+ and (SO_4^{2-}) . The positive hydrogen ions are attracted to the negative cathode, where they pick up an electron, normally combine to form a molecule, and are released as a free gas. The negative sulfate ions go to the positive anode, where they are neutralized, but then react with water to produce more sulfuric acid and release oxygen. The sulfuric acid acts as a catalyst, and the result is the splitting up of water into hydrogen and oxygen.



If an electrode such as titanium, tantalum, or palladium (which reacts exothermically with hydrogen) is used as the cathode, the metal becomes charged with hydrogen. Instead of being released as free gas, the hydrogen enters the metal and diffuses into the lattice. Hydride derivatives can form with concentrations of up to two hydrogen atoms per metal atom.

See also: Nuclear Fusion.

Electron

The electron is a subatomic particle (symbol e^-) that has a negative electric charge and has a mass that is approximately 1/1,836 that of the proton. The properties of the electron include a natural spin. Like all elementary particles, electrons exhibit properties of particles and waves and can collide with other particles and be diffracted.

Electrons play an essential role in numerous physical phenomena, such as electricity, magnetism, chemistry, thermal conductivity, and (most important in the current context) radioactivity, especially radioactive decay. Electrons radiate or absorb energy in the form of photons when they are accelerated.

Electrons can be created through beta decay of radioactive isotopes and in high-energy collisions. The antiparticle of the electron is the positron which is identical to the electron except that it carries electrical a positive charge. When an electron collides with a positron, both particles can cease to exist thereby producing gamma ray photons.

See also: Radioactive Decay, Positron, Radioactivity,

Electronic Waste

Electronic waste (e-waste or WEEE – waste electrical and electronic equipment) is a waste type consisting of any broken or unwanted electrical or electronic appliance. It is a point of concern considering that many components of such equipment are considered toxic and are not biodegradable.

Electronic waste includes computers, entertainment electronics, mobile phones, and other items that have been discarded by their original users. While there is no generally accepted definition of electronic waste, in most cases electronic waste consists of electronic products that were used for data processing, telecommunications, or entertainment in private households and businesses that are now considered obsolete, broken, or irreparable. Despite its common classification as a waste, disposed electronics are a considerable category of secondary resource due to their significant suitability for direct reuse (for example, many fully functional computers and components are discarded during upgrades), refurbishing, and material recycling of its constituent raw materials (listed below). The potential for electronic waste as a resource thus preempts its potentially hazardous qualities.

Electronic waste is a valuable source for secondary raw materials, if treated properly; however, if not treated properly, it is a major source of toxins. Rapid technology change, low initial cost, and even planned obsolescence have resulted in a fast-growing problem around the globe. Technical solutions are available, but in most cases, a legal framework, a collection system, logistics, and other services need to be implemented before a technical solution can be applied.

See also: Domestic Waste, Industrial Waste, Waste.

Electrostatic Precipitator

Electrostatic precipitation is the separation of liquid or solid particles from a gas stream by the action of electrically charged wires and plates. The precipitator is used for the collection of dusts, mists, and fumes which are defined by size or type, thus: (i) dust, which are solid particles from 0.1 to 100 microns (0.1 to 100) μm in diameter, (ii) mist, which is liquid droplets suspended in a gas, and (iii) fumes, which are solid or liquid particles formed by condensation from a vapor. The precipitator uses electrostatic forces which are induced by electrostatic charging of the solids and then dropping them under freefall between oppositely charged electrodes. The electrostatic field of the electrodes deflects the solids, depending on the charge, into separate receiving bins. A third is the ion exchange concept, which depends on the ability of molecules to ionize into positively charged and negatively charged ions which are removed from waste streams by replacing them with more desirable ions.

The basic components of a precipitator are the discharge (or corona) electrode, the collection electrode (plates), and the precipitator shell. Other components are the dust hopper, high-voltage equipment, and gas distributors. Suspended particles are charged by collisions with the negative ions passing through the zone between the corona and the collection electrode. Movement of the particles to the collection electrode is governed by the interaction of the electric field and charged particles in the moving gas stream.

The dust cake is then collected from the plate by striking it with rappers. The dust collection efficiency is a strong function of dust resistivity. In general, particles in a gas stream are charged by a high-voltage discharge electrode and collected at collection plates of opposite polarity. Particles of high resistivity create the most difficulty in collection. Because resistivity varies with temperature, this can be an important parameter. Conditioning agents such as sulfur trioxide have been used to lower resistivity. Other important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include high-voltage pulse energization to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of high efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations.

The dust collection efficiency is a strong function of dust resistivity. In general, particles in a gas stream are charged by a high-voltage discharge electrode and collected at collection plates of opposite polarity. Particles of high resistivity create the most difficulty in collection. Because resistivity varies with temperature, this can be an important parameter. Conditioning agents such as sulfur trioxide have been used to lower resistivity. Other important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles).

There are two main types of precipitators which are (i) high-voltage, single-stage precipitators which combine an ionization and a collection step which are commonly referred to as Cottrell precipitators and (ii) low-voltage, two-stage precipitators which use a similar principle; however, the ionizing section is followed by collection plates.

The majority of electrostatic precipitators installed are the plate type. Particles are collected on flat, parallel surfaces that are 8 to 12 in. (20 to 30 cm) apart, with a series of discharge electrodes spaced along the centerline of two adjacent plates. The contaminated gases pass through the passage between the plates, and the particles become charged and adhere to the collection plates. Collected particles are usually removed by rapping the plates and deposited in bins or hoppers at the base of the precipitator.

Tubular precipitators consist of cylindrical collection electrodes with discharge electrodes located on the axis of the cylinder. The contaminated gases flow around the discharge electrode and up through the inside of the cylinders. The charged particles are collected on the grounded walls of the cylinder. The collected dust is removed from the bottom of the cylinder. Tubular precipitators are often used for mist or fog collection or for adhesive, sticky, radioactive, or extremely toxic materials.

In the oil shale industry, electrostatic precipitators could be used in several operations, including mine ventilation and the second-stage cleaning of dust laden streams from crushers and conveyors.

See also: Gas Cleaning, Gas Processing, Gas Treating, Dust, Dust Control, Electrostatic Processes.

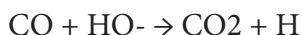
Emissions and Effluents

Whatever the type of energy source (alternate or alternative, non-renewable or renewable) is used to produce fuels and energy, the capacity of the environment to absorb the effluents and other impacts of energy technologies is not unlimited, as some would have us believe. The environment should be considered to be an extremely limited resource, and discharge of chemicals into it should be subject to severe constraints. Indeed, the declining quality of many raw materials dictates that more material must be processed to provide the needed products. And the growing magnitude of the effluents from industrial processes has moved above the line where the environment has the capability to absorb such effluents without disruption. Thus, the general prognosis for environmental protection through an increased awareness of environmental issues is not pessimistic and can be looked upon as being quite optimistic.

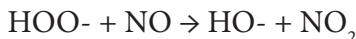
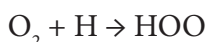
In terms of gaseous emissions, the control of nitrogen oxides is achieved, to date, mainly through modification of the combustion process, and other methods, including various flue gas treating processes are being developed. Indeed, it is anticipated that flue gas control technologies may achieve significantly higher control of gaseous emissions than currently being recorded. In fact, the current flue gas desulfurization techniques are capable of removing approximately 90% w/w of the sulfur. However, it is extremely important that there is an understanding of the various types of emissions that escape to the atmosphere, as well as to the other constituents of the surrounding environment.

A number of inorganic emissions enter the atmosphere as the result of human activities. The most common of these emissions are sulfur dioxide (SO₂), nitric oxide (NO), and nitrogen dioxide (NO₂). Other inorganic gaseous emissions include ammonia (NH₃), hydrogen sulfide (H₂S), chlorine (Cl₂), hydrogen chloride (HCl), and hydrogen fluoride (HF), as well as other oxides of nitrogen. Because of carbon monoxide emissions from internal combustion engines, the highest levels of this gas tend to occur in congested urban areas at times specific times, such as during heavy road traffic periods (rush hours). Carbon monoxide emissions from automobiles may be lowered by employing a leaner air-fuel mixture, i.e., an air-fuel in which the weight ratio of air to fuel is relatively high. Current automobiles use catalytic exhaust reactors to cut down on carbon monoxide emissions and nitrogen oxide emissions. But, in more general terms, there is the need to increase the efficiency of automobile transportation (Nivola and Crandall, 1995) which, hopefully, would reduce the noxious emissions into the atmosphere.

If the carbon monoxide escapes to the atmosphere, it is generally agreed that it is removed from the atmosphere by reaction with hydroxyl radical:



This reaction is accompanied by other chemical reactions which lead to the regeneration of more hydroxyl radicals:



Soil microorganisms act to remove carbon monoxide from the atmosphere.

The sulfur cycle involves primarily hydrogen sulfide, sulfur dioxide, sulfur trioxide, and sulfates. Sulfur compounds enter the atmosphere to a large extent through human activities, primarily as sulfur dioxide from the combustion, or processing, of sulfur-containing fuels. Non-anthropogenic sulfur enters the atmosphere largely as hydrogen sulfide from volcanoes and from the biological decay of organic matter and reduction of sulfate.

Organic emissions may have a strong effect upon atmospheric quality. The effects of such emissions in the atmosphere may be divided into two major categories which are (i) direct effects, such as effects caused by exposure to the

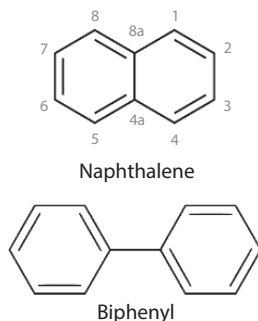
emissions, and (ii) the formation of secondary pollutants, especially smog (a mixture of smoke and fog). Because of their widespread use in fuels, hydrocarbon derivatives predominate among organic atmospheric pollutants.

Crude oil products, primarily gasoline, are the source of most of the anthropogenic hydrocarbon emissions found in the atmosphere. The Clean Air Act of 1990 has already impacted the gasoline markets of the United States (Miller, 1994). Additives and reformulation have already been implemented in some case to meet regulations and emission standards required for compliance, and gasoline will continue to be reformulated.

Alkane derivatives are among the more stable hydrocarbon derivatives in the atmosphere. Because of their high vapor pressures, alkanes with 6 or fewer carbon atoms are normally present as gases; alkanes with 20 or more carbon atoms are present as aerosols or are adsorbed on to atmospheric particles. Alkanes with 6 to 21 carbon atoms per molecule may be present either as vapor or particles, depending upon conditions.

Alkenes enter the atmosphere from a variety of processes, including emissions from internal combustion engines and turbines, foundry operations, and crude oil refining. In addition to the direct release of alkenes, these hydrocarbon derivatives are commonly produced by the partial combustion and cracking (thermal decomposition) at high temperatures of alkanes, particularly in the internal combustion engine. Unlike alkanes, alkenes are highly reactive in the atmosphere, especially in the presence of nitrogen oxides, hydroxyl radicals, and sunlight. In addition, the reaction of molecular oxygen to the resulting radical results in the formation of the extremely reactive hydroperoxyl radical. These radicals then participate in chain reactions such as those involved in the formation of smog.

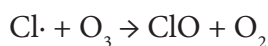
Single-ring aromatic compounds are important constituents of lead-free gasoline, which has largely replaced leaded gasoline. In fact, derivatives of naphthalene (which has two fused, conjugated, aromatic rings) and several compounds containing two or more unconjugated rings have been detected as atmospheric pollutants.



Polynuclear aromatic hydrocarbon derivatives (Table 2.4) are present as aerosols in the atmosphere because of their extremely low vapor pressure. The partial combustion of coal, which has an atomic hydrogen-to-carbon ratio close to or less than 1, is a source of polynuclear aromatic compounds which have considerable toxicity (Lee et al., 1981).

Carbonyl compounds, consisting of aldehyde derivatives ($RCHO$) and ketone derivatives (R^1COR^2 where R^1 and R^2 are the same or different hydrocarbon groups), enter the atmosphere from a large number of sources and processes. These include direct emissions from internal combustion engine exhausts, incinerator emissions, spray painting, polymer manufacture, printing, petrochemicals manufacture, and lacquer manufacture. Formaldehyde ($HCHO$) and acetaldehyde (CH_3CHO) are produced by microorganisms, and acetaldehyde is emitted by various types of vegetation.

As expected from their low vapor pressures, the lower-boiling organic halogen compounds are the most likely to be found in the atmosphere. The most abundant organic chlorine compounds in the atmosphere are methyl chloride (CH_3Cl) and carbon tetrachloride (CCl_4). Also found are methylene chloride (CH_2Cl_2), methyl bromide (CH_3Br), bromoform ($CHBr_3$), assorted chlorofluorocarbons and halogen-substituted ethylene compounds, such as trichloroethylene ($CHCl=CCl_2$), vinyl chloride ($CH_2=CHCl$), perchloroethylene ($CCl_2=CCl_2$), and ethylene dibromide (CH_2BrCH_2Br). Many of these types of chlorocarbon derivatives and chlorofluorocarbon derivatives have been implicated in the halogen-atom-catalyzed destruction of atmospheric ozone which filters out cancer-causing ultra-violet radiation from the sun.



Although inert in the lower atmosphere, chlorofluorocarbon derivatives undergo photodecomposition by the action of high-energy ultraviolet radiation in the stratosphere to release chlorine atoms which then react with ozone to produce chlorine monoxide.

While organic sulfur derivatives are not highly significant as atmospheric contaminants on a large scale, organic sulfur compounds can cause local pollution problems – not the least of which is the highly objectionable odor. Major sources of organic sulfur compounds in the atmosphere include microbial degradation, wood pulping, volatile matter evolved from plants, animal wastes, packing house and rendering plant wastes, starch manufacture, sewage treatment, and crude oil refining.

Aromatic amines are widely used as chemical intermediates, antioxidants, and curing agents in the manufacture of polymers (rubber and plastics), drugs, pesticides, dyes, pigments, and inks. A large number of heterocyclic nitrogen compounds have been reported in tobacco smoke, and it is inferred that many of these compounds can enter the atmosphere from burning vegetation. Coke ovens are another major source of these compounds. In addition to the derivatives of pyridine, some of the heterocyclic nitrogen compounds are derivatives of pyrrole.

Particulate matter is a term that has come to stand for (liquid or solid) particles in the atmosphere which may be organic or inorganic and originate from a wide variety of sources and processes. As one example, particulate matter is produced from mineral matter in a carbonaceous fuel that is converted during combustion to finely divided inorganic material referred to as fly ash. This low density ash can be carried out of the stack with the hot exhaust gases and also has the ability to adsorb polynuclear aromatic hydrocarbon derivatives. Furthermore, the practice of burning any finely divided carbonaceous fuel can contribute to fly ash emissions which are composed of several chemical species (such as arsenic, cadmium, mercury, thallium, and zinc compounds) that are of environmental significance in soil, in water, and in the atmosphere (Kothny, 1973). Indeed, the United States Clean Air Act of 1990 requires the evaluation of several trace elements with a view to the banning of such emissions.

The particulate matter (PM, also referred to as particulates, atmospheric aerosol particles, atmospheric particulate matter, or suspended particulate matter, SPM) is a collection of microscopic particles of solid particles (or even liquid matter) suspended in the air. The term aerosol commonly refers to the particulate/air mixture, as opposed to the particulate matter alone. The source of the particulate matter can be natural or anthropogenic. The particulate matter can have impacts on climate and precipitation that adversely affect human health in ways additional to direct inhalation. The particulate matter is often categorized by size of the particles such as (i) coarse particles, which are designated PM_{10} with a diameter of 10 micrometers (10 microns, 10 μm ; (1 micron = 1 meter $\times 10^{-6}$) or less, (ii) fine particles, designated $PM_{2.5}$ with a diameter of 2.5 μm or less, (iii) ultrafine particles, $PM_{0.1}$, and (iv) soot. All of the aforementioned particles are inhalable to congregate in the lungs and, therefore, are a hazard to human health.

Soot as an airborne contaminant in the environment has many different sources, all of which are results of thermal decomposition, particularly pyrolysis. The sources include soot from coal combustion, internal-combustion engines, power-plant boilers as well as a variety of boilers, waste incineration local field (agricultural) burning, house fires, forest fires, fireplaces, and furnaces. These exterior sources also contribute to the indoor environment sources such as smoking of plant matter, cooking, oil lamps, candles, quartz/halogen bulbs with settled dust, and defective furnaces.

The formation of soot depends strongly on the fuel composition. The rank ordering of the soot forming tendency (also referred to as the propensity for soot formation) of fuel components is:

Naphthalene derivatives > benzene derivatives > aliphatic derivatives

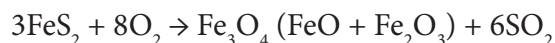
However, the order of the soot-forming propensity within any of the above chemical hydrocarbon groups varies dramatically and is dependent on the structural type of the hydrocarbon derivative and the heteroatom (N, O, S) content.

Thus, particulate matter, which ranges in size from approximately one-half millimeter down to molecular dimensions, may consist of either solids or liquid droplets. Atmospheric aerosols are solid or liquid particles smaller than 100 microns in diameter. Pollutant particles in the 0.001 to 10 micron range are commonly suspended in the air near sources of pollution, such as the urban atmosphere, industrial plants, highways, and power plants. The small, solid particles include carbon black, silver iodide (AgI), combustion nuclei, and sea-salt nuclei, and the larger particles include cement dust, windblown soil dust, foundry dust, and any pulverized solid fuel – thus, the need for dust control is strong (Mody and Jakhete, 1988). On the other hand, the liquid particulate matter (mist) includes raindrops,

fog, and sulfuric acid mist and some particles are of biological origin, such as viruses, bacteria, bacterial spores, fungal spores, and pollen. Atmospheric particles undergo a number of processes in the atmosphere. Sedimentation and scavenging by raindrops and other forms of precipitation are the major mechanisms for particle removal from the atmosphere; particulate matter also reacts with atmospheric gases.

Dispersion aerosols, such as dusts, formed from the disintegration of larger particles are usually above 1 micron in size. Typical processes for forming dispersion aerosols include evolution of dust from coal grinding, formation of spray in cooling towers, and blowing of dirt from dry soil. Many dispersion aerosols originate from natural sources, such as sea spray, windblown dust, and volcanic dust. However, a vast variety of human activities break up material and disperse it to the atmosphere.

Metal oxides constitute a major class of inorganic particles in the atmosphere. These are formed during the combustion of fuels that containing metals. For example, particulate iron oxide is formed during the combustion of pyrite-containing coal:



Organic vanadium in residual fuel oil is converted to particulate vanadium oxide. Part of the calcium carbonate in the ash fraction of coal is converted by heat to calcium oxide and is emitted to the atmosphere through the stack:



A common process for the formation of aerosol mists involves the oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic substance that accumulates atmospheric water to form small liquid droplets:



In the presence of basic air pollutants, such as ammonia (NH_3) or calcium oxide (CaO), the sulfuric acid (H_2SO_4) reacts to form the ammonium or calcium salts. Under conditions of low humidity, water is lost from these droplets and a solid aerosol is formed.

A significant portion of organic particulate matter is produced by internal combustion engines. These products may include nitrogen-containing compounds and oxidized hydrocarbon polymers. Lubricating oil and its additives may also contribute to organic particulate matter.

Particulate carbon as soot, carbon black, coke, and graphite originates from auto and truck exhausts, heating furnaces, incinerators, power plants, and steel and foundry operations and composes one of the more visible and troublesome particulate air pollutants. Because of its good adsorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. Particulate carbon surfaces may catalyze some heterogeneous atmospheric reactions, including the important conversion of sulfur dioxide to sulfate.

Another mineral worthy of note as a pollutant is asbestos which is of considerable concern as an air pollutant because when inhaled, the fibrils can lodge in human tissue and cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinomas (cancer originating with the air passages in the lungs).

By way of definition, asbestos is the name given to a group of six fibrous silicate minerals, typically those of the serpentine group. Chemically, asbestos is a group of impure magnesium silicate minerals and colors may be white, gray, green, or brown, and is noncombustible. Serpentine asbestos is the mineral chrysotile, a magnesium silicate with strong and flexible fibers. Spinning is possible with the longer fibers. Amphibole asbestos includes various silicates of magnesium, iron, calcium, and sodium. The fibers are generally brittle and cannot be spun, but are more resistant to chemicals and to heat than serpentine asbestos. Because asbestos has long been indicated in asbestosis (similar to silicosis) and, in more recent years, considered a carcinogen, several countries have issued regulations that restrict its use. For many years, it has been used in fireproof fabrics, brake lining, gaskets, roofing, insulation, paint fillers, reinforcing agents in rubber and plastics, and in electrolytic diaphragm cells.

As a side note, talc is a clay mineral that is composed of hydrated magnesium silicate $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$ and has been known to occur with asbestos.

Some of the metals found predominantly as particulate matter in polluted atmospheres are known to be hazardous to human health. All of these except beryllium are so-called heavy metals. Lead is the toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at a toxic level; mercury ranks second. Others include beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid). Arsenic can have a significant effect on the environment, whether the metalloid is released to the land, the water, or the air (Nriagu, 1994a 1994b).

Atmospheric mercury (Hg^0) is of concern because of its toxicity, volatility, and mobility. Some atmospheric mercury is associated with particulate matter. One means by which mercury can enter the atmosphere is as volatile elemental mercury from coal combustion (ASTM D3684). Volatile organic mercury compounds such as dimethyl mercury $[(\text{CH}_3)_2\text{Hg}]$ and methyl mercury salts, such as methyl mercury bromide (CH_3HgBr) , are also encountered in the atmosphere. With the reduction in the use of leaded fuels, atmospheric lead is of less concern than it used to be.

A significant natural source of radionuclides in the atmosphere is radon, a noble gas product of radium decay. Radon may enter the atmosphere as either of two isotopes, ^{222}Rn (half-life: 3.8 days) and ^{220}Rn (half-life: 54.5 seconds). Both are alpha emitters in decay chains that produce a series of daughter products and terminate with stable isotopes of lead. The initial decay products, isotopes of polonium (^{218}Po and ^{216}Po), are nongaseous and adhere readily to atmospheric particulate matter. Therefore, some of the radioactivity detected in these particles is of natural origin.

One of the more serious problems in connection with radon is that of radioactivity originating from uranium mine tailings that have been used in some areas as backfill, soil conditioner, and a base for building foundations. Radon produced by the decay of radium exudes from foundations and walls constructed on tailings. Some medical authorities have suggested that the rate of birth defects and infant cancer in areas where uranium mill tailings have been used in residential construction are significantly higher than normal.

The combustion of fossil fuels introduces radioactivity into the atmosphere in the form of radionuclides contained in fly ash. Large coal-fired power plants lacking ash-control equipment may introduce up to several hundred millicuries of radionuclides into the atmosphere each year, far more than either an equivalent nuclear or an equivalent oil-fired power plant.

The radioactive noble gas krypton (^{85}Kr) has a half-life on the order of 10.3 years and is emitted into the atmosphere by the operation of nuclear reactors and the processing of spent reactor fuels. In general, other radionuclides produced by reactor operation are either chemically reactive and can be removed from the reactor effluent or have such short half-lives that a short time delay prior to emission prevents them from leaving the reactor.

The above-ground detonation of nuclear weapons can add large amounts of radioactive particulate matter to the atmosphere. Although there are general agreements between several nations to cease and desist from testing nuclear devices in the atmosphere, not all nations agree to this proposition.

It is considered likely that most of the environmental impact of mineral resource development (including the hazards of coal mining, gaseous emissions, and acid precipitation) could be substantially abated. A considerable investment in retrofitting or replacing existing facilities and equipment might be needed. However, replacing coal with natural gas, which releases less carbon dioxide per unit of energy, is at best a short-term solution.

Minimizing the carbon dioxide emissions from many mineral resources (which must also include emissions of hydrogen sulfide) would require revamping of the current technology. But it is possible, and a conscious goal must be to improve the efficiency with which the resources are transformed and consumed and by shifting to alternative products.

In terms of the production of transportation fuels from biomass sources, ethanol (ethyl alcohol; grain alcohol) is a major biomass fuel, but in the current market conditions, it remains significantly more expensive than gasoline. The widespread use of biomass (alcohol) fuel is constrained by the size of the resource base from which they are produced. There is also the argument that methyl alcohol (methanol) produced from natural gas releases as much carbon dioxide as does gasoline. The counterargument is that methanol-fueled engines have a greater potential for improvements than gasoline engines do (for example, they can function at higher levels of compression than have heretofore been attempted).

There is the need for the systematic identification and evaluation of the potential impacts of proposed projects, plans, programs, policies, or legislative actions upon the physical-chemical, biological, cultural, and socioeconomic

components of the environment. Also known as environmental impact assessment, it also includes the consideration of measures to mitigate undesirable impacts. The primary purpose of environmental impact assessment is to encourage consideration of the environment in planning and decision making and ultimately to arrive at actions that are environmentally compatible.

Impact assessment refers to the interpretation of the significance of anticipated changes related to the proposed project. Impact interpretation can be based upon the systematic application of the definition of significance, as described earlier. For some types of anticipated impacts, there are specific numerical standards or criteria that can be used as a basis for impact interpretation. Examples include airquality standards, environmental noise criteria, surface-water and groundwater quality standards, and wastewater discharge standards for particular facilities. The latter is especially true since the quality of wastewater can vary with the nature of the facility.

In this context, it is necessary to consider the impacts related to the biological environment and the potential significance of the loss of particular habitats, including wetland areas (Dennison and Berry, 1993). Another basis for assessment is public input, which could be received through the scoping process or through public participation programs.

Identifying and evaluating potential impact mitigation measures should also be an activity in the process of environmental impact assessment. Mitigation can be defined as the sequential consideration of measures such as (i) avoiding the impact by not taking a certain action or parts of an action, (ii) minimizing impacts by limiting the degree or magnitude of the action and its implementation, (iii) rectifying the impact by repairing, rehabilitating, or restoring the affected environment, (iv) reducing or eliminating the impact over time by preservation and maintenance operations during the life of the action, and (v) compensating for the impact by replacing or providing substitute resources or environments. Examples of mitigation measures include pipeline routing to avoid archeological resources, inclusion of pollution-control equipment on airborne and liquid discharges, reductions in project size, revegetation programs, wildlife protection plans, erosion control measures, remediation activities, and creation of artificial wetlands.

A key activity in environmental impact assessment is associated with selecting the proposed action from alternatives that have been evaluated (Inhaber, 1982). In public projects, there is considerable emphasis on the evaluation of alternatives; in fact, various regulations (Majumdar, 1993) indicate that the analysis of alternatives represents the heart of the impact assessment process. Conversely, for many private developments, the range of alternatives may be limited. Even so, there are still potential alternative measures that could be evaluated, including those relating to project size and design features even if location alternatives are not available.

Environmental impact studies need to address a minimum of two alternatives, and can include more than fifty alternatives. Typical studies address three to five alternatives. The minimum number usually represents a choice between the construction and operation of a project versus project rejection. The alternatives may encompass a wide range of alternate considerations such as (i) site location, (ii) design of a site, (iii) construction, operation, and decommissioning options, (iv) project size, (v) phasing in of operational units, (vi) timing of the construction, operation, and decommissioning activities, and (vii) the option that related to a non-project.

All of the aforementioned arguments for and against the use of resources do not belie the obvious. Mineral resources, including fossil fuel resources, will continue to be sources of valuable products for the next several decades. They must be used judiciously insofar as they are sources of pollutants, many of which are gases and which must not be released to the atmosphere.

Obviously, much work is needed to accommodate the change to a different fuel source. In the meantime, there must be serious efforts to improve efficient usage and working to ensure that there is no damage to the environment. Such is the nature of resource development and use and the expectancy of environmental protection.

See also: Emission Control

Emission Control

Emission control by direct flame incineration systems (thermal combustion) is widely used to reduce the amounts of hydrocarbon vapors, aerosols, and particulate in gas streams. These systems are also used to remove odors and reduce the opacity of plumes from ovens, dryers, stills, cookers, and refuse burners.

The operation consists of ducting the process exhaust gases to a combustion chamber where direct-fired burners burn the gases to their respective oxides. Catalytic incineration is also used for the same purpose. The chief difference is that the combustion chamber is filled with a catalyst. On contact with the catalyst, certain components of the process gases are oxidized.

The use of a catalyst allows more complete combustion at lower temperatures, thus reducing fuel consumption and allowing the use of less expensive furnace construction. However, catalysts are generally selective and may not destroy as many contaminants as direct flame incineration. In addition, because of the potential for catalyst fouling and poisoning, gas streams may need to be cleaned of smoke, particulate, heavy metals, and other catalyst poisons. Condensation is usually combined with other air pollution control systems to reduce the total pollutant load on more expensive control equipment. When used alone, condensation often requires costly refrigeration to achieve the low temperatures needed for adequate control.

Several methods can be used for cooling the gas streams. In surface condensers, the coolant does not contact the vapor or condensate; condensation occurs on a wall separating the coolant and the vapor. Most surface condensers are common shell-and-tube heat exchangers. The coolant normally flows through the tubes; the vapor condenses on the cool outside tube surface as a film and is drained away to storage or disposal.

Contact condensers usually cool the vapor by spraying a liquid, at ambient temperature or slightly cooler, directly into the gas stream. They also act as scrubbers in removing vapors that do not normally condense. The use of quench water as the cooling medium results in a waste stream that must be contained and treated before discharge.

The equipment used for contact condensation includes simple spray towers, high-velocity jets, and barometric condensers. Contact condensers are, in general, less expensive, more flexible, and more efficient in removing organic vapors than surface condensers. On the other hand, surface condensers recover marketable condensate and present no waste disposal problem. Surface condensers require more auxiliary equipment and need more maintenance.

Condensers have been widely used (usually with additional equipment) in controlling organic emissions from crude oil refining, petrochemical manufacturing, dry cleaning, decreasing, and tar dipping. Refrigerated condensation processes are being used for the recovery of gasoline vapors at bulk terminals and service stations.

See also: Emissions and Effluents.

Emulsification

An emulsion is a mixture of two or more liquids that are usually immiscible. Examples include crude oil and water which can form an oil-in-water emulsion, wherein the oil is the dispersed phase, and water is the dispersion medium or a water-in-oil emulsion, wherein the water is the dispersed phase, and the oil is the dispersion medium. The physical structure of an emulsion is based on the size of the droplets – most emulsions contain droplets with a mean diameter of more than approximately 1 μm (1 micron, 1×10^{-6} meter); however, mini-emulsions and nano-emulsions can be formed with droplet sizes in the 100 to 500 nm (nanometer, 1×10^{-9} meter) range, and with proper formulation, highly stable microemulsion can be prepared having droplets as small as a few nanometers.

When the water and an organic liquid (such as bio-oil) are combined by emulsification, two emulsion structures are possible. The oil phase may become dispersed throughout the aqueous phase to produce an oil-in-water (o/w) emulsion. Alternatively, the aqueous phase may become dispersed throughout the oil phase to produce a water-in-oil (w/o) emulsion. In general, an emulsion tends to exhibit the characteristics of the external phase. Two emulsions of similar composition can have different properties, depending on their structure. For example, an o/w emulsion can be diluted with water, colored with water-soluble dye and has a relatively high electrical conductivity compared to a w/o system. The latter is best diluted with oil and colored with oil-soluble dye. Many factors can influence the type of emulsion formed when two phases are mixed, including the type of emulsifying agent used, the relative proportions of the phases, and the method of preparation employed.

Emulsions with more complex structures, known as *multiple emulsions*, may also be produced. These may have oil-in-water-in-oil (o/w/o) or water-in-oil-in-water (w/o/w) structures. The latter structure has the most applications. w/o/w emulsions may be produced in two stages. First, a w/o emulsion is produced by homogenization using a hydrophobic agent. This is then incorporated into an aqueous phase using a hydrophilic agent. In such a multiple emulsion, the oil layer is thin and water can permeate through it due to an osmotic pressure gradient between the

two aqueous phases. This property is used in certain applications including prolonged drug delivery systems, drug overdose treatments, and nutrient administration for special dietary purposes.

In a two-phase system, free energy exists at the interface between the two immiscible liquids, due to an imbalance in the cohesive forces of the two materials. Because of the interfacial tension, there is a tendency for the interface to contract. Thus, if a crude emulsion is formed by mixing two immiscible liquids, the internal phase will take the form of spherical droplets, representing the smallest surface area per unit volume. If the mixing is stopped, the droplets coalesce to form larger ones and eventually, the two phases will completely separate. To form an emulsion, this interfacial tension has to be overcome. Thus, energy must be introduced into the system. This is normally achieved by agitating the liquids. The greater the interfacial tension between the two liquids, the more energy required to disperse the internal phase. Reducing this interfacial tension will facilitate the formation of an emulsion. This is one important role of emulsifying agents. Another function of these agents is to form a protective coating around the droplets of the internal phase and thus prevent them from coalescing and destabilizing the emulsion.

The stability of an emulsion refers to the ability of the emulsion to resist change in form and properties over time. There are three types of instability in emulsions: (i) flocculation, (ii) creaming, and (iii) coalescence. Flocculation occurs when there is an attractive force between the droplets, so they form a flocculant mass (flocs) in the fluid through precipitation or aggregation of suspended particles. Creaming occurs when the droplets rise to the top of the emulsion under the influence of buoyancy. Coalescence occurs when droplets collide and combine to form a larger droplet, so the average droplet size increases over time. Use of a surface-active agent (surfactant) can increase the stability of an emulsion so that the size of the droplets does not change significantly with time and the emulsion is then defined as a *stable emulsion*.

This demulsification process can be slowed with the help of emulsifiers which are surface-active substances with strong hydrophilic properties that are used to eliminate the prolonged effects of spills in which emulsions are formed. Emulsifiers help to stabilize emulsions and promote dispersing the phase oil to form microscopic (invisible) droplets which may accelerate the decomposition of the pollutant in the water.

The formation of an emulsion based on water and chemicals is less likely than in the case of water and organic chemicals. Nevertheless, the properties of chemicals as a function of the solubility in water is important because of the potential use of the chemicals to break, for example, an o/w emulsion that forms after a crude oil spill into the aquasphere and the potential to aid in the clean-up process.

See also: Water.

Emulsifying Agents

Emulsifying agents are chemicals with good emulsifying properties and have molecular structures which contain both polar and nonpolar groups. Polar groups have an affinity for water, i.e., are hydrophilic, while nonpolar groups are hydrophobic. If there is a small imbalance between the polar and nonpolar groups in the molecules of a substance, it will be adsorbed at the interface between the phases of an emulsion. These molecules will become aligned at the interface so that the polar groups will point toward the water phase, while the nonpolar groups will point toward the oil phase. By bridging the interface in this way, they reduce the interfacial tension between the phases and form a film around the droplets of the internal phase, thus stabilizing them. A substance in which the polar group is stronger will be more soluble in water than one in which the nonpolar group predominates. Such a substance will tend to promote the formation of an o/w emulsion. However, if the nonpolar group is dominant, the substance will tend to produce a w/o emulsion. If the polar and nonpolar groups are grossly out of balance, the substance will be highly soluble in one or other of the phases and will not accumulate at the interface. Such materials do not make good emulsifying agents.

The emulsifying capability of an agent may be classified according to the hydrophile-lipophile balance (HLB) in its molecules. This is defined as the ratio of the weight percentage of hydrophilic groups to the weight percentage of hydrophobic groups in the molecule. Hydrophile-lipophile balance values for emulsifying agents range from 1 to 20. Agents with low values, 3 to 6, promote the formation of w/o emulsions, while those with high values, 8 to 16, favor the formation of o/w types. Agents with even higher hydrophile-lipophile balance values are used in detergents and solubilizers.

Protein, phospholipids, and sterols, which occur naturally in many types of biomass, act as emulsifying agents. A wide range of manufactured agents is available, both ionic and nonionic. Ionic emulsifiers often react with other oppositely charged particles such as hydrogen and metallic ions to form complexes. This may result in a reduction in solubility and emulsifying capacity. Hydrocolloids such as pectin and gums are often used to increase the viscosity of emulsions to reduce separation of the phases under gravity (creaming).

See also: Emulsification.

Endothermic Reaction

An endothermic reaction is a process in which heat is absorbed. The heat has to be supplied to the system from the surroundings. This heat is transferred to the surroundings. A thermo-neutral reaction process is one that neither requires heat from the surroundings nor gives off energy to the surroundings.

These terms are usually applied to chemical reactions. A chemical reaction can only be one of these three terms at once. A reaction that is exothermic will be endothermic if run backward and vice-versa.

In a chemical reaction, reactants are converted into products by the breaking and making of chemical bonds. Bond breaking requires energy, while bond making releases energy. The balance between the two gives a positive or negative energy change for the reaction, and chemical reactions are classed as being either *endothermic*, with a positive energy change, or *exothermic*, with a negative energy change.

In an endothermic reaction, more energy is taken breaking bonds than is released making them, so the reaction proceeds with a net absorption of energy. In an exothermic reaction, the reverse is true and energy is released.

Thus, an endothermic reaction is a process in which energy (heat, light) is absorbed or requires heat input into the system (Figure E-1). The heat has to be supplied to the system from the surroundings or from a heat source.

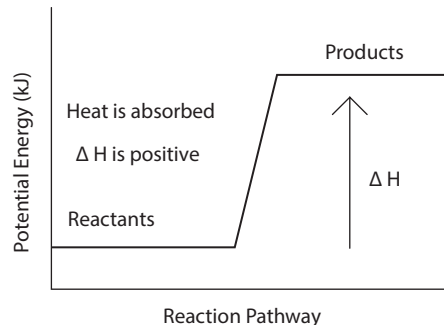


Figure E-1 Representation of an endothermic reaction in which the heat content of the products is greater than the heat content of the reactants.

A *thermoneutral* reaction process is one that neither requires heat from the surroundings nor gives off energy to the surroundings.

Endothermic reactions are in the minority, and most chemical reactions release energy. Although an endothermic reaction usually needs energy to initiate the reaction, some endothermic reactions occur without initiation. Compounds formed by endothermic reactions have stored or potential chemical energy in their bonds, which may be released spontaneously in an explosion, such as in the case with chlorates, perchlorates, and nitrates.

See also: Exothermic Reaction.

Energy

Energy (from whatever the sources – fossil fuel sources or alternate sources) appears in many different forms, including electricity, light, heat, chemical energy, and motional (or kinetic) energy. An important scientific

discovery in the 19th century was that energy is conserved which means that energy can be converted from one form to another but that the total amount of energy must stay the same. Mass is also familiar, though sometimes it is referred to, rather inaccurately, as weight. On the surface of the Earth, mass and weight are often thought of as being the same thing, and they do use the same units – something that weighs 1 kilogram has a mass of 1 kilogram – but in reality, weight is the force that a mass experiences in the gravity of the Earth. An object always has the same mass, even though in outer space, it might appear to be weightless. Mass, like energy, is conserved.

Energy Balance

The energy balance is the difference between the energy produced by a fuel and the energy required to obtain it through agricultural processes, drilling, refining, and transportation.

All biomass goes through at least some of these steps: it needs to be grown, collected, dried, fermented, and burned. All of these steps require resources and an infrastructure. The total amount of energy input into the process compared to the energy released by burning the resulting ethanol fuel is known as the energy balance (net energy gain).

Energy balance estimates are not easily produced; thus numerous such reports have been generated that are contradictory. For instance, the production of ethanol from sugarcane, which requires a tropical climate to grow productively, returns from 8 to 9 units of energy for each unit expended, as compared to corn which only returns approximately about 1 to 2 units of fuel energy for each unit of energy expended. As a positive example, biodiesel (depending upon the production train) has a positive energy balance: for energy unit of energy required to produce biodiesel, 2.5 to 3.2 units of energy are gained. In addition, carbon dioxide, a greenhouse gas, is emitted during fermentation and combustion. However, this is canceled out by the greater uptake of carbon dioxide by the plants as they grow to produce the biomass. When compared to gasoline, depending on the production method, ethanol releases less greenhouse gases.

See also: Energy Content, Ethanol, Fossil Fuels.

Energy Conservation

Energy is a primary input to development. Fossil and nuclear fuels are fast depleting in different countries. Energy conservation is the decision and practice of using less energy. Turning off the light when leaving the room, unplugging appliances when they are not in use, and walking instead of driving are all examples of energy conservation. The two main reasons people conserve energy are to gain more control over the demand on the Earth's natural resources. Energy conservation is an important part of the transition to clean, renewable energy. By promoting initiatives to encourage and assist the community to adopt less energy-intensive lifestyles, the shift to 100% renewable energy can be an easier transition and the environmental impact can be reduced.

Energy conservation is the first step to a sustainable future because of the low risk and high reward. If there is a movement to decrease energy demand through energy conservation, reliance on nonrenewable energy sources can be reduced while at the same time expanding proliferation of renewable energy. Energy conservation is only part of the solution, especially in a growing economy. Energy conservation focuses on changing human behavior to utilize energy in a more efficient manner. Energy conservation behavioral changes can be made for little or no cost. Sustainable energy is the peak of the pyramid and so must be the last part of the pyramid to be built.

Energy conservation appears to be one of the most effective methods to increase and use energy efficiency, and to decrease energy consumption and greenhouse gas (GHG) emissions in various sectors. Therefore, many countries have recently started improving enterprising energy conservation programs to decrease the energy intensity of the country's infrastructure.

Energy conservation is now an important social topic. There is an expanding body of knowledge in the literature focused on promoting consumers in decreasing their personal carbon footprint in their domestic context. However, most of the research in the workplace focuses on optimizing formalized production processes and investing in energy-efficient equipment.

In sustainable development, energy resources create little or no wastes to be emitted into the environment and they cause only waste emissions having no or minimal negative impact on the environment. However, all resource use leads to some degree of environmental problem, and limitations imposed on sustainable development by environmental emissions can be in part overcome through increased efficiency. A large number of potential solutions to environmental problems related to the harmful pollutant emissions have been worked out, recently. A significant one among them is energy conservation. Energy conservation activities have been improved because of its indirect contribution to the prevention of environmental pollution.

Energy conservation is commonly listed as the main method of response. Governments should improve and apply energy conservation policies to decrease the impacts of environmental problem. The creation of any energy conservation policy could lead to a reduction in economic growth and eventually to a fall in income and employment.

Energy Content

Thermal energy is released from organic materials as the carbohydrates and other hydrocarbon derivatives (lignin and volatile chemicals) are ultimately reduced to carbon dioxide and water. The amount of usable thermal energy that can be obtained from fuel is known as the higher heating value (HHV). By contrast, the lower heating value (LHV) is equivalent to the HHV of the fuel minus heat required to vaporize the liquid water of the fuel. Interestingly, on a dry, ash-free basis, most biomass has approximately the same energy content (HHV) of 8,000 to 8,500 British thermal units per pound (Btu/lb). However, the practical heating value of biomass, as received, varies considerably due to differences in the content of ash-forming minerals and moisture.

Chemical composition, and therefore heat content, varies by plant component and biomass type. For example, the relative proportions of carbohydrates and other hydrocarbon derivatives vary between the two types of woody biomass: softwoods and hardwoods. Carbohydrates carry a lower heat content (6,000 to 7,000 Btu/lb) than the other hydrocarbon derivatives in organic matter (such as lignin at 10,000 to 12,000 Btu/lb) but are easier to hydrolyze into higher-value fuels and chemicals in fermentation processes than other hydrocarbon derivatives. Softwoods generally contain a higher percentage of volatile hydrocarbon derivatives, in the form of gums and resins, than do hardwoods. As a result, softwoods often, but not always, have higher heat content than hardwoods. In addition, bark often has higher lignin content than wood, which is one reason why its HHV is higher than wood of the same species.

Fuels with low heat content increase feedstock transportation costs per unit of usable thermal energy, thereby affecting the economics of biomass power generation. While it may be possible to pay less per ton for a feedstock with a lower HHV, it is likely to cost the same amount to transport a ton of low-energy fuel as it would to transport a ton of high energy-density material.

In addition, the energy content of biomass fuels per unit volume can increase feedstock quantity requirements for combustion and gasification. This affects storage, handling, and processing needs and the sizing of boiler and gasification systems. For example, using biomass fuels with low energy densities per unit volume may require a larger boiler vessel to achieve the same heat output as a boiler system run with a biomass fuel that has a higher energy density.

See also: Energy Balance.

Energy Crops

Energy crops are agricultural crops grown specifically for their energy value (fuel value) (Table E-2) and include food crops such as corn and sugarcane, and nonfood crops such as poplar trees and switchgrass.

Table E-2 Examples of the properties of straw and energy crops.

Property	Cereal straw	Energy crops
Proximate analysis		
Ash, % w/w	3-10	6.2-7.5
Moisture, % w/w	14-25	15-20
Volatile matter, % w/w w/	70-81	>70
Ash melting point, oC	700-1,000	700-1,200
Elemental analysis		
C, % w/w	45-48	45.5-46.1
H, % w/w	5.0-6.0	5.7-5.8
N, % w/w	0.4-0.6	0.50-1.0
O, % w/w	36-48	41-44
S, % w/w	0.05-0.2	0.08-0.13
Cl, % w/w	0.14-0.97	0.09
K, % w/w	0.69-1.3	0.3-0.5
Ca, % w/w	0.1-0.6	9

Energy crops such as grasses, miscanthus oilseed crops, short rotation woody crops, residual herbaceous biomass, starch crops, sugar crops, and switchgrass can be converted to liquid biofuels by thermochemical and biochemical conversion process. The most appropriate biomass crop for energy production is one that can be harvested dry and has a perennial growth habit (no need for annual planting or tillage) to minimize cultivation costs. Low input of fertilizers and other chemicals when growing these plants helps to improve the energy efficiency. It is also important that plants can convert solar energy efficiently. Two major pathways of photosynthesis are the C3 and C4 pathway. In general, the C3 assimilation path is adapted to operate under low temperature (15-20°C) whereas in the C4 metabolic pathway, species are more efficient converters in high light level and high temperature situations. Tropical grasses, such as sugar cane, maize, also miscanthus and sweet sorghum are C4 plants.

C4 plants can generate a theoretical maximum dry matter yield of 22 tons per acre in a year compared with 13 tons per acre from normal C3 temperate crops. However, C4 plants can only generate such a yield under hot climate conditions. In temperate climate, C3 plants might be more suitable. For example, short rotation forestry suitable for energy production under temperate climate is generally the C3 species – such as willow and poplar.

In order to determine suitability of energy crops to grow them in a chosen area, the following factors should be considered: the energy balance, agronomic factors such as crop yields, soils and climate, energy output per hectare, and effective utilization of all of the components of the crop at the processing stage. Calorific value, amount of ash the plants produce when used, as well as their moisture content are of a crucial importance for energy production.

Generally, the C4 crops such as Miscanthus are more suitable for arable lands whereas C3 crops can be grown on marginal land. In order to make the crop growing process environmentally friendly, a transportation distance should be as short as possible and should not exceed 40 km.

Markets for biomass crops have been slow to develop. The concept of co-firing biomass in existing power plants continues to show promise. Electric utilities are interested in co-firing biomass as a way to meet the renewable energy mandate, should it become law. In addition, there are air quality benefits from biomass fuels. Since biomass fuels are low in sulfur and nitrogen – SO_x which causes acid rain and NO_x which contributes to smog is lower in smokestack emissions when biomass fuels are burned with coal.

There are many opportunities for producing fuel from agricultural crops and crop residues. Possible end products include ethanol, vegetable oil, and solid cellulosic fuels. Ethanol can be produced from any grain, root, fruit, or juice crop containing fermentable carbohydrates. It also can be made from crops, residues, or wood that contain cellulose or other long-chain carbohydrates which can be hydrolyzed to fermentable sugars.

Vegetable oils are produced from numerous oil seed crops. Some of these oils have been evaluated in other laboratories as substitutes for diesel fuel. While all vegetable oils have high energy content, most require some processing to assure safe use in internal combustion engines.

The simplest form of agricultural biomass energy use involves direct combustion of cellulosic crops or residues, such as hay, straw, or corn fodder, to heat space or produce steam. Such fuels are useful for heating farm buildings and small commercial buildings in rural areas and for drying crops. Ideally, energy crops should be produced on land not needed for food production. This use should not increase the erosion hazard or cause other environmental damage.

On the other hand, a variety of crops can be grown specifically to provide sources of energy, and once established, a stand of perennial biomass/energy crop is expected to remain productive for a period of 6 years or more.

Thus, perennial crops that regenerate annually from buds at the base of the plant offer the greatest potential for energy-efficient production. These include (i) short rotation coppice, (ii) miscanthus, (iii) reed canary grass, (iv) cordgrass, (v) switchgrass, (vi) reed plants, (vii) Jerusalem artichoke, and (viii) sorghum.

Short rotation coppice (or SRC) refers to fast-growing deciduous trees which are grown as energy crops, such as willow and poplar trees. The species of short rotation coppice that are most suitable, and therefore most popular, for use as energy crops are poplar and willow (and possibly also birch) because they both require deep, moisture-retentive soils for proper growth. Willow, in particular, is able to endure periods of water logging and is therefore better suited to wetter soils.

Miscanthus is a hardy perennial rhizomatous grass that produces a crop of bamboo-like cane up to 14 feet tall. Rhizomatous implies that it spreads naturally by means of underground storage organs (rhizomes). Miscanthus can grow up to ten feet tall and theoretically can give an annual harvest of up to 12 tons per acre. Like other bioenergy crops, the harvested stems of miscanthus may be used as fuel for production of heat and electric power, or for conversion to other useful products such as ethanol. Miscanthus is high in lignin and lignocellulose fiber and uses the C4 pathway. It can be grown in a cool climate and on many types of arable land. Miscanthus does not require a big input of fertilizers due to its capability to recycle large amounts of nutrients.

Miscanthus has a similar calorific value per unit weight as wood and therefore could possibly be used in the same power plant or those designed for agricultural residues.

Reed canary grass is a robust C3 perennial grass, widely distributed across temperate regions of Europe, Asia, and also North America. It usually grows in damp areas.

This rhizomatous grass can grow up to six feet in height and usually flowers in June and July. Reed canary grass is usually harvested once per year either by mowing or baling using a high density baler. Crop duration of 10 years or more may be possible. Due to its low moisture content, canary grass (those harvested in spring) can be easily converted to pellets, briquettes, and powder.

Cordgrasses are perennial grasses from Western Europe, Africa and North America. They are pioneer colonists of muddy coastal salt flats, spreading by means of rhizomes to form clumps and mats which help to reduce erosion and reclaim land from the sea. Cordgrasses are expected to be able to produce good yields of biomass in poor soil conditions.

Switchgrass is a perennial sod-forming grass with thick strong stems. The advantages of switchgrass as an energy crop are that it is fast-growing, remarkably adaptable, and high-yielding. Further advantages of switchgrass are that it can be harvested, using conventional equipment, either annually or semi-annually for 10 years or more before replanting is needed and that it is able to reach deep into the soil for water and use water very efficiently.

The utilization of energy crops such as switchgrass (*Panicum virgatum*, L., Poaceae) is a concept with great relevance to current ecological and economic issues on a global scale. Development of a significant national capacity to utilize perennial forage crops, such as switchgrass as biofuels, could provide an important new source of energy from perennial cropping systems, which are compatible with conventional farming practices, would help reduce degradation of agricultural soils, and lower national dependence on foreign oil.

Reed plants are a potentially prolific producer of biomass, capable of yielding 20-25 t per ha of dry matter annually for a number of years. They can grow up to 6 m, are spread by means of stout rhizomes and stolons, and are commonly found in swampy ground and shallow water throughout temperate and subtropical areas.

The high-fructose syrups that can be derived from the tubers produced by the Jerusalem artichoke may be used for the production of ethanol and other industrial raw materials. Jerusalem Artichokes also produce a large amount of top growth which may also prove to be a useful source of biomass for energy purposes.

Sorghum is an annual tropical grass with large genetic variation that is a crop with the potential for energy production. Sweet sorghum has been selected for its sugar content and is normally grown for molasses production. Forage sorghum has been selected for high yields of reasonably good-quality animal feed. Sorghum varieties producing tall plants with large stems make the best candidates for biomass production. Both sweet and forage sorghum have a high potential for lodging. Lodging can result in harvest problems with ensuing loss of yield from both initial and ratoon crops.

Sweet sorghums produce sugar syrups which could form the basis of fermentation processes for methane or ethanol production, and some of the forage types of the plant may be suitable for biomass production.

Hemp is an annual short day, C3 plant with a high cellulose and lignin content in its stems and a high fat and protein content in its seeds. The entire plant consisting of bast fibers, leaves, seeds, and processable remains can be used as a solid fuel when compacted. The stalk contains a strong and durable fiber. The average height is on the order of 7 feet, but the hemp stalk can reach up to 12 feet in height. For the energetic use, the whole hemp crop is harvested.

Hemp can be easily planted and cultivated, but its growing is prohibited in many countries as it can be used as a drug. The plants vegetative period is approximately 100 days, with the main growth period in summer months followed by flowering in toward the end of summer. The yields are high, but the high plant moisture content can create storage problems. Two different harvesting technologies are available for the energy use of the whole hemp crop.

The first is the whole-fiber-technology where, with a modified chopping technology, the hemp culm is cut into 24 to 24-inch lengths. The straw stays for four weeks on the field for drying before the bales are pressed. Another technology is wet harvesting. This technology includes the chopping of the crops followed by silaging. For combustion, it is necessary to press the hemp silage into bales to reduce the water content of the fuel.

All crops, including some biennial, permanent, and multiannual crops, are produced for energy purposes. Energy is generated by burning plants grown for the purpose, often after the dry matter is pelletized. Energy crops are used for firing power plants, either alone or co-fired with other fuels. Alternatively, they may be used for heat or combined heat and power (CHP) production.

See also: Cordgrass and Switchgrass, Jerusalem Artichoke, Miscanthus, Reed Plants, Residual Herbaceous Biomass, Short Rotation Coppice, Sorghum.

Energy Crops – Grasses

Grasses are usually herbaceous plants with narrow leaves growing from the base. They include the true grasses of the Poaceae (or Gramineae) family, as well as the sedges (Cyperaceae) and the rushes (Juncaceae). The true grasses include cereals, bamboo and the grasses of lawns (turf), and grassland. Sedges include many wild marsh and grassland plants, and some cultivated ones such as water chestnut (*Eleocharis dulcis*) and papyrus sedge (*Cyperus papyrus*). Most of the interest in grass biomass tends to focus on economics, but there is a list of traits that should be considered and valued when evaluating a potential solid biomass energy source. These traits are beneficial to society in general, or impact the suitability of biomass for a farm operation.

Miscanthus is a tall hardy perennial rhizomatous grass that produces a crop of bamboo-like cane up to 4 meters tall and which has been evaluated in Europe during the past 5-10 years as a new bioenergy crop. Like other energy crops, the harvested stems of miscanthus may be used as fuel for production of heat and electric power, or for conversion to other useful products such as ethanol.

The fact is that miscanthus *rhizomatous* implies that it spreads naturally by means of underground storage organs (rhizomes). Miscanthus can grow up to ten feet tall and theoretically can give an annual harvest of up to 12 tons per acre. Like other bioenergy crops, the harvested stems of miscanthus may be used as fuel for production of heat and electric power, or for conversion to other useful products such as ethanol. Miscanthus is high in lignin and

lignocellulose fiber and uses the C4 pathway. It can be grown in a cool climate and on many types of arable land. Miscanthus does not require a big input of fertilizers due to its capability to recycle large amounts of nutrients. Miscanthus has a similar calorific value per unit weight as wood and therefore could possibly be used in the same power plant or those designed for agricultural residues.

Switchgrass is a perennial sod-forming grass with thick strong stems. The advantages of switchgrass as an energy crop are that it is fast-growing, remarkably adaptable, and high-yielding. Further advantages of switchgrass are that it can be harvested, using conventional equipment, either annually or semi-annually for 10 years or more before replanting is needed and that it is able to reach deep into the soil for water and use water very efficiently.

Switchgrass is a perennial grass native to North America. Switchgrass makes for a great energy crop because it grows fast, capturing lots of solar energy and turning it into chemical energy which it stores as cellulose.

Switchgrass has the potential to be a versatile bioenergy feedstock since the energy content is comparable to that of wood with significantly lower initial moisture content. Switchgrass is a very suitable substrate and produces high ethanol yield using current simultaneous saccharification and fermentation technology. Extensive analysis of ash and alkali content of switchgrass indicates that it typically has relatively low alkali content and should have low slagging potential in coal-fired combustion systems. As an agro-fiber source for pulping, switchgrass has a relatively high cellulose content, low ash content, and good fiber length-to-width ratios. Switchgrass reaches its full yield potential after the third year planted, producing approximately 6 to 8 tons per acre; that is 500 gallons of ethanol per acre.

The utilization of energy crops such as *switchgrass* (*Panicum virgatum*, L., Poaceae) is a concept with great relevance to current ecological and economic issues on a global scale. Development of a significant national capacity to utilize perennial forage crops, such as switchgrass as biofuels, could provide an important new source of energy from perennial cropping systems, which are compatible with conventional farming practices, would help reduce degradation of agricultural soils, and lower national dependence on foreign oil.

See also: Energy Crops.

Energy Crops – Oilseed Crops

Oilseed crops are diverse in the plant kingdom and belong to several families and include plants such as soybean and canola (rapeseed). Soybean and groundnut are members of the legume family Fabaceae (Leguminosae) and have been grown in rotation, with other crops benefiting from the nitrogen fixation feature of soybean and groundnut. Rhizobium and related genera in the root nodules of legumes fix atmospheric nitrogen. Much of the nitrogen remains in the soil and is available for subsequent crops. These crops have the ability to produce oil within the seeds, and the oil can be pressed out of the ripe seed.

Oilseed crops are grown throughout the world for use as vegetable and industrial oils, spices, and birdfeed. In a region dominated by winter and spring wheat, the acceptance and production of another crop requires that it has an agronomic benefit to the cropping system. Canola (*Brassica* sp.), mustard (*B. juncea* and *Sinapis alba* L.), and flax (*Linum usitatissimum* L.) are well-adapted to cool, short-season conditions found on the Canadian prairies and northern Great Plains border states of the United States. Sunflower (*Helianthus annuus* L.) and safflower (*Carthamus tinctorius* L.) are better adapted to the longer growing season and warmer temperatures.

Thus, oilseeds constitute an important group of commercial crops, and rapeseed mustard, groundnut, sesame, linseed, and castor, are major crops.

See also: Canola Oil, Energy Crops, Soybeans.

Energy Crops – Residual Herbaceous Biomass

Herbaceous energy crops such as the woody, perennial, rhizomatous grasses like miscanthus offer the advantage of an annual harvest.

Residual herbaceous biomass (straw) is the main residual herbaceous material for energy application. As it is a residual product, its availability for energy purposes is driven by the cereal markets and does not have autonomous market behavior. In addition, farms consume significant quantities of straw internally – as bed material for livestock,

grain drying, etc. Some straw is also chaffed and returned back to the field as a soil ameliorator. The net straw yield per hectare for energy application also depends on the crop, the grain yield per hectare, climate and cultivation conditions, etc. Nevertheless, one can roughly estimate that the average straw yield per hectare is approximately 50 to 65% of the grain yield per hectare from cereals and oilseeds.

Similar to herbaceous crops, straw usually has lower moisture content than woody biomass. Conversely, it has a lower calorific value, bulk density, ash melting point and higher content of ash, and problematic inorganic component such as chlorine, potassium, and sulfur, which cause corrosion and pollution. The last two drawbacks can be relatively easily overcome by leaving straw on the field for a while. In such a way, rainfall “washes” it naturally from a large part of potassium and chlorine. Alternatively, fresh straw can be directly shipped to the gasification plant, where it is washed by dedicated facilities at moderate temperatures (50 to 60°C; 120 to 140°F). Due to washing, the initially low moisture content of straw becomes higher in both cases and hence, a mandatory drying is applied afterwards. In both cases also, the content of corrosive components is reduced, but not completely taken out. In order to decrease handling costs, straw and dedicated herbaceous energy crops are usually baled before being shipped to the gasification plant. The weight and the size of bales depend on the baling equipment and on the requirements of the gasification plant.

In starch crops, most of the six-carbon sugar units are linked together in long, branched chains (starch). Yeast cannot use these chains to produce ethanol. The starch chains must be broken down into individual six-carbon units or groups of two units. The starch conversion process is relatively simple because the bonds in the starch chain can be broken in an inexpensive manner by the use of heat and enzymes, or by a mild acid solution.

See also: Energy Crops.

Energy Crops – Short Rotation Woody Crops

Short rotation energy crops that are harvested on a cycle of anything from 2 to 20 years, depending on the crop and the system, and herbaceous energy crops that are harvested annually.

Short rotation woody crops (short rotation coppice or SRC) refers to fast-growing deciduous trees which are grown as energy crops, such as willow and poplar trees. The species of SRC that are most suitable, and therefore most popular, for use as energy crops are poplar and willow (and possibly also birch) because they both require deep, moisture-retentive soils for proper growth. Willow, in particular, is able to endure periods of water logging and is therefore better suited to wetter soils.

See also: Energy Crops.

Energy Crops – Sugar Crops

Sugar crops include a variety of plants such as fodder beets, fruit crops, Jerusalem artichokes, sugar beets, sugar cane, and sweet sorghum. Interest in ethanol production from such agricultural crops has prompted the development of sugar crops that have not been cultivated on a widespread commercial basis in many countries. Preparation is basically a crushing and extraction of the sugars which the yeast can immediately use. But sugar crops must be dealt with fairly quickly before their high sugar and water content causes spoilage. Because of the danger of such spoilage, the storage of sugar crops is not practical.

The fodder beet is a high-yielding forage crop obtained by crossing two other beet species, sugar beets and mangolds. It is similar in most agronomic respects to sugar beets. The attraction of this crop lies in its higher yield of fermentable sugars per acre relative to sugar beets and its comparatively high resistance to loss of fermentable sugars during storage.

Fruit crops (e.g., grapes, apricots, peaches, and pears) are another type of feedstock in the sugar crop category. Typically, fruit crops such as grapes are used as the feedstock in wine production. These crops are not likely to be used as feedstocks for production of fuel-grade ethanol because of their high market value for direct human consumption. However, the co-products of processing fruit crops are likely to be used as feedstocks because fermentation is an

economical method for reducing the potential environmental impact of untreated wastes containing fermentable sugars.

The Jerusalem artichoke has shown excellent potential as an alternative sugar crop. A member of the sunflower family, this crop is native to North America and well-adapted to northern climates. Like the sugar beet, the Jerusalem artichoke produces sugar in the top growth and stores it in the roots and tuber. It can grow in a variety of soils, and it is not demanding of soil fertility. The Jerusalem artichoke is a perennial plant; small tubers left in the field will produce the next season's crop, so no ploughing or seeding is necessary.

Although sugar beets are grown in many areas of the U.S., they must be rotated with non-root crops: (1 beet crop per 4 year period is the general rule). While beet by-products cannot provide fuel for the distillery, the beet pulp and tops are excellent feed in wet or dry form. Or the tops may be left on the field for fertilizer and erosion control.

Sugar cane produces high yields per acre of both sugar and crop residue which are strong points of sugar cane production. The crop residue, called bagasse, is used in Brazil to provide heat for the distilleries.

Sweet sorghum is a name given to varieties of a species of sorghum. This crop has been cultivated on a small scale in the past for production of table syrup, but other varieties can be grown for production of sugar. The most common types of sorghum species are those used for production of grain. Sweet sorghum can be considered as an energy crop, because it can be grown in all continents, in tropical, sub-tropical, temperate regions as well as in poor-quality soils. Sweet sorghum is a warm-season crop that matures earlier under high temperatures and short days. Sweet sorghum is an extraordinarily promising multifunctional crop not only for its high economic value but also for its capacity to provide a very wide range of renewable energy products, industrial commodities, food, and animal feed products. Sweet sorghum biomass is rich in readily fermentable sugars, and thus it can be considered as an excellent raw material for fermentative hydrogen production. Integrated production of several crops (sweet sorghum/sugar-cane/sweet sorghum corn/sweet sorghum/ sweet potatoes), and simultaneous processing of the full crop components (starch, sugar, lignocellulosic) can improve the global economics of bioenergy schemes considerably in view of a viable production of bioethanol.

See also: Energy Crops.

Energy Density

The energy density is the amount of energy stored in a system or region of space per unit volume. It may also be used for energy per unit mass, though the accurate term for this is specific energy. Often, only the useful or extractable energy is measured. Energy per unit volume has the same physical units as pressure.

There are several different types of energy content. One is the theoretical total amount of thermodynamic work that can be derived from a system, with a given temperature and pressure for the surroundings – this is referred to as the exergy of the system.

In terms of energy content and energy density, there are two kinds of heat of combustion: (i) the higher value (HHV), or gross heat of combustion, includes all the heat released as the products cool to room temperature and whatever water vapor is present condenses, and (ii) the lower value (LHV), or net heat of combustion, does not include the heat which could be released by condensing water vapor, and may not include the heat released on cooling all the way down to room temperature.

See also: Heat Content.

Energy-Efficiency Ratio

Fuel efficiency is the efficiency of a process that converts chemical potential energy contained in a carrier fuel into energy. Overall fuel efficiency may vary per device, which in turn may vary per application, and this spectrum of variance is often illustrated as a continuous energy profile.

The energy efficiency ratio is a number which represents the energy stored in a fuel as compared to the energy required to produce, process, transport, and distribute that fuel. The specific energy content of a fuel is the heat

energy obtained when a certain quantity is burned (such as a gallon, liter, kilogram). The specific energy content is also known as the heat of combustion.

There exist two different values of specific heat energy for the same batch of fuel – one is the high (or gross) heat of combustion, and the other is the low (or net) heat of combustion. The high value is obtained when, after the combustion, the water in the exhaust is in liquid form. For the low value, the exhaust has all the water in vapor form (steam). Since water vapor gives up heat energy when it changes from vapor to liquid, the high value is larger since it includes the latent heat of vaporization of water. The difference between the high and low values is significant, approximately 8 or 9%. This accounts for most of the apparent discrepancy in the heat value of gasoline.

Energy Production from Crops

There are four basic types of processes used to generate energy from crops: direct combustion, gasification, pyrolysis, and anaerobic digestion.

Direct combustion involves burning the energy crop and then using the resulting hot combustion gases to raise steam. The steam is, in turn, used to drive a steam turbine which drives a generator to produce electricity. The conversion efficiency from energy crop to energy is fairly low, especially for small systems, but this is balanced by the relatively low capital cost of direct combustion systems and the fact that the technology is tried and tested. Furthermore, using the waste heat produces much better efficiencies and economics.

Combustion facilities can burn many types of biomass fuel, including wood, agricultural residues, wood pulping liquor, municipal solid waste (MSW), and refuse-derived fuel. Combustion technologies convert biomass fuels into several forms of useful energy for commercial or industrial uses: hot air, hot water, steam, and electricity.

A furnace is the simplest combustion technology. In a furnace, biomass fuel burns in a combustion chamber, converting biomass into heat energy. As the biomass burns, hot gases are released. These hot gases contain approximately 85% of the fuel's potential energy. Commercial and industrial facilities use furnaces for heat, either directly or indirectly through a heat exchanger in the form of hot air or water.

A biomass-fired boiler is a more adaptable direct combustion technology because a boiler transfers the heat of combustion into steam. Steam can be used for electricity, mechanical energy, or heat. Biomass boilers supply energy at low cost for many industrial and commercial uses.

Pile burners consist of cells, each having an upper and a lower combustion chamber. Biomass fuel burns on a grate in the lower chamber, releasing volatile gases. The gases burn in the upper (secondary) combustion chamber, and pile burners must be shut down periodically to remove ash.

Although capable of handling high-moisture fuels and fuels mixed with dirt, pile burners have become obsolete with the development of more efficient combustion designs with automated ash removal systems.

In a stationary or traveling grate combustor, an automatic feeder distributes the fuel onto a grate, where the fuel burns. Combustion air enters from below the grate. In the stationary grate design, ashes fall into a pit for collection. In contrast, a traveling grate system has a moving grate that drops the ash into a hopper.

Fluidized-bed combustors burn biomass fuel in a hot bed of granular material, such as sand. Injection of air into the bed creates turbulence resembling a boiling liquid. The turbulence distributes and suspends the fuel. This design increases heat transfer and allows for operating temperatures below 972°C (1,700°F), reducing nitrogen oxide (NO_x) emissions. Fluidized-bed combustors can handle high-ash fuels and agricultural biomass residue.

Conventional combustion equipment is not designed for burning agricultural residues. Straw and grass contain alkali (potassium and sodium) compounds, which are also present in all annual crops and crop residues and in the annual growth of trees and plants. During combustion, alkali combines with silica, which is also present in agricultural residues. This reaction causes slagging and fouling problems in conventional combustion equipment designed for burning wood at higher temperatures.

Volatile alkali lowers the fusion temperature of ash. In conventional combustion equipment having furnace gas exit temperatures above 780°C (1,450°F), combustion of agricultural residue causes slagging and deposits on heat transfer surfaces. Specially designed boilers with lower furnace exit temperatures could reduce slagging and fouling from combustion of these fuels. Low-temperature gasification may be another method of using these fuels for efficient energy production while avoiding the slagging and fouling problems encountered in direct combustion.

Combustion facilities that produce electricity from steam-driven turbine-generators have a conversion efficiency on the order of 17 to 25%. Using a boiler to produce both heat and electricity (cogeneration) improves overall system efficiency to as much as 85%. That is, cogeneration converts 85% of the fuel's potential energy into useful energy in two forms: electricity and steam heat.

Two cogeneration arrangements, or cycles, are possible for combining electric power generation with industrial steam production. Steam can be used in an industrial process first and then routed through a turbine to generate electricity. This arrangement is called a bottoming cycle. In the alternate arrangement, steam from the boiler passes first through a turbine to produce electric power. The steam exhaust from the turbine is then used for industrial processes or for space and water heating. This arrangement is called a topping cycle.

The direct-fired gas turbine is another combustion technology for converting biomass to electricity. In this technology, fuel pretreatment reduces biomass to a particle size of less than 2 millimeters and a moisture content of less than 25%. Then, the fuel is burned with compressed air. Cleanup of the combustion gas reduces particulate matter before the gas expands through the turbine stage. The turbine drives a generator to produce electricity.

Co-firing biomass as a secondary fuel in a coal-burning power plant using high-sulfur coal could help reduce sulfur dioxide and nitrogen oxide emissions. Also, co-firing decreases net carbon dioxide emissions from the power plant (if the biomass fuel comes from a sustainable source). Co-firing may require wood fuel preparation or boiler modifications to maintain boiler efficiency.

Gasification is a high temperature process which produces gas which can then be used in an internal combustion engine or fuel cell.

Briefly, gasification was used as long ago as the early 1800s. The process was rather crude, and the fuel was most often coal. The gas product (town gas) was used for heating and lighting. For example, the gas was piped to street lights as early as 1846 in England.

The gasification process produces a fuel gas from crops by heating them under carefully controlled temperature, pressure, and atmospheric conditions. A key to gasification is using less air or oxygen than is usually found in combustor. The product (biogas or fuel gas), like natural gas, can be burned in high-efficiency gas turbines.

The gasifier is the heart of the gasification process. Gasifiers are designed to process the fuel in a variety of ways consistent with the type of fuel, the end use of the gas, the size of the process, and the source of oxygen. The oxygen may be introduced as a pure gas or may come from air or steam. Some gasifiers operate under pressure; others do not.

The simplest type of gasifier is the fixed bed countercurrent gasifier. The biomass is fed at the top of the reactor and moves downwards as a result of the conversion of the biomass and the removal of ashes. The air intake is at the bottom, and the gas leaves at the top. The biomass moves in countercurrent to the gas flow, and passes through the drying zone, the distillation zone, reduction zone, and the oxidation zone.

The major advantages of this type of gasifier are its simplicity, high charcoal burn-out, and internal heat exchange leading to low gas exit temperatures and high gasification efficiency. In this way also, fuels with high moisture content (up to 50 % w/w) can be used. The major drawbacks are the high amounts of tar and pyrolysis products because the pyrolysis gas is not led through the oxidation zone. This is of minor importance if the gas is used for direct heat applications, in which the tars are usually burnt. In case the gas is used for engines, gas cleaning is required, resulting in problems of tar-containing condensates.

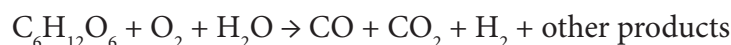
In the conventional downdraft gasifier (sometimes called the co-flow gasifier), biomass is fed at the top of the reactor and air intake is at the top or from the sides. The gas leaves at the bottom of the reactor, so the fuel and the gas move in the same direction. The pyrolysis gasses are lead through the oxidation zone (with high temperatures) and/or more or less burnt or cracked. Therefore, the producer gas has low tar content and is suitable for engine applications. In practice, however, a tar-free gas is seldom if ever achieved over the whole operating range of the equipment. Because of the lower level of organic components in the condensate, downdraft gasifiers suffer less from environmental objections than updraft gasifiers.

Successful operation of a downdraft gasifier requires drying the biomass fuel to a moisture content of less than 20%. The advantage of the downdraft design is the low tar content of the producer gas. However, the disadvantages of the downdraft gasifier are (i) the high amounts of ash and dust particles in the gas, (ii) the inability to operate on a number of unprocessed fuels, often pelletization or briquetting of the biomass is necessary, (iii) the outlet gas has a high temperature leading to a lower gasification efficiency, and (iv) the moisture content of the biomass must be less than 25% by weight.

A more recent development is the open core gasifier design for gasification of small sized biomass with high ash content. The producer gas is not tar-free; it contains approx. 0.05 kg tar per kg gas. In the open core gasifier, the air is sucked over the whole cross section from the top of the bed. This facilitates better oxygen distribution since the oxygen will be consumed over the whole cross section, so that the solid bed temperature will not reach the local extremes (hot spots) observed in the oxidation zone of conventional gasifiers due to poor heat transfer. Moreover, the air nozzles in conventional gasifiers generate caves and create obstacles that may obstruct solid flow – especially for solids of low bulk such as rice husk. On the other hand, the entry of air through the top of the bed creates a downward flow of the pyrolysis gases, and transports the tar products to the combustion zone. Thus, flow problems due to the caking of rice husk caused by back mixing of tar are avoided.

The gasification process is amenable to a variety of biomass feedstocks such as waste rice hulls, wood waste, grass, and the dedicated energy crops. Gasification is a clean process with few air emissions and, when crops are used as the feedstock, little or no ash.

In the gasifier, biomass is converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds by applying heat under pressure in the presence of steam and a controlled amount of oxygen. The biomass produces synthesis gas.



The above reaction uses glucose as a surrogate for cellulose. Biomass has highly variable composition and complexity, with cellulose as one major component.

The gasification process could play a significant role in meeting the goal of greenhouse gas mitigation. It is likely that both in the transition phase to a hydrogen economy and in the steady state, a significant fraction of hydrogen might be derived from domestically abundant crops.

In addition to the co-firing applications of crops (and other biomass) biomass with coal, biomass can provide up to 15% of the total energy input of the fuel mixture. Such concepts address greenhouse gas mitigation by co-firing biomass and coal to offset the losses of carbon dioxide to the atmosphere that are inherent in coal combustion processes (even with the best-engineered capture and storage of carbon). Since growth of biomass fixes atmospheric carbon, its combustion leads to no net addition of atmospheric carbon dioxide even if vented. Thus, co-firing of crops or crop residues (or other biomass with coal) in an efficient coal gasification process, affording the opportunity for capture and storage of carbon dioxide, could lead to a net reduction of atmospheric carbon dioxide. Cheaper, though less plentiful, biomass residue could supplant crops as gasifier feedstock leading to a less significant impact on the environment than would farming bioenergy crops.

Along similar lines, willow biomass crops have been shown to be a good fuel for farm-based power production using advanced gasification technology. The fuel gas can be used for generating electricity, using micro-turbines modified to operate on low-BTU gas, or for other farm energy needs. Willow biomass was found to make a fuel for ash-rejection gasifiers with a predicted net gasification efficiency of approximately 85%. Analysis showed that developing a method to co-gasify willow with various amounts of low-cost wastes, such as dairy farm animal waste, can be an excellent way to reduce the fuel cost, to increase the overall fuel availability, and to help work around problems resulting from seasonal availability of bioenergy crops. Co-gasification of dairy farm wastes along with willow offers an economical way to dispose of the wastes and manage nutrient flows on a dairy farm.

Agricultural residues can be divided into two groups, and these are (i) crop residues and (ii) agro-industrial residues. Crop residues are plant materials left behind in the farm after removal of the main crop produce. The remaining materials could be of different sizes, shapes, forms, and densities like straw, stalks, sticks, leaves, haulms, fibrous materials, roots, branches, and twigs.

Due to high energy content, straw is one of the best crop residues for solid biofuels. However, straw has several disadvantages – it has a higher ash content, which results in lower calorific value. In order to improve its bulk density, the straw is generally baled before transportation. Straw burning requires a specific technology. There are four basic types of straw burners: those that accept shredded, loose straw; burners that use densified straw products such as pellets, briquettes or cubes, and straw logs; small, square bale burners and round bale burners. To be suitable for heat and electricity production, straw should not have a large content of moisture, preferably not more than 20% as

the moisture reduces the boiler efficiency. Also, straw color as well as straw chemistry should be considered before burning as it indicates the quality of the straw.

The agro-industrial residues are by-products of the post-harvest processes of crops such as cleaning, threshing, sieving, and crushing. These could be in the form of husk, dust, and straw. Furthermore, the quantity of agricultural residues produced differs from crop to crop and is affected by soil type and irrigation conditions. Production of agricultural residues is related to the corresponding crop production and ratio between the main crop produce and the residues, which varies from crop to crop and, at times, with the variety of the seeds in one crop itself. Thus, for known amounts of crop production, it may be possible to estimate the amounts of agricultural residues produced using the residue-to-crop ratio.

Most crop or agricultural residues are not found throughout the year but are available only at the time of harvest. The amount available depends upon the harvesting time, storage-related characteristics, and the storage facility.

Pyrolysis is a medium temperature method which produces gas, oil, and char from crops which can then be further processed into useful fuels or feedstock.

Pyrolysis is often considered to be the gasification of biomass in the absence of oxygen. However, the chemistry of each process may differ significantly. In general, biomass does not gasify as easily as coal, and it produces other hydrocarbon compounds in the gas mixture exiting the gasifier; this is especially true when no oxygen is used. As a result, typically an extra step must be taken to reform these hydrocarbon derivatives with a catalyst to yield a clean syngas mixture of hydrogen, carbon monoxide, and carbon dioxide.

Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles and a short hot vapor residence time in the reaction zone. Several reactor configurations have been shown to assure this condition and to achieve yields of liquid product as high as 75% based on the starting dry biomass weight. They include bubbling fluid beds, circulating and transported beds, cyclonic reactors, and ablative reactors.

Fast pyrolysis of biomass produces a liquid product, pyrolysis oil or bio-oil that can be readily stored and transported. Pyrolysis oil is a renewable liquid fuel and can also be used for production of chemicals. Fast pyrolysis has now achieved a commercial success for production of chemicals and is being actively developed for producing liquid fuels. Pyrolysis oil has been successfully tested in engines, turbines, and boilers, and been upgraded to high-quality hydrocarbon fuels.

Direct hydrothermal liquefaction involves converting biomass to an oily liquid by contacting the biomass with water at elevated temperatures (300 to 350°C) with sufficient pressure to maintain the water primarily in the liquid phase (12 to 20 MPa) for residence times up to 30 minutes. Alkali may be added to promote organic conversion. The primary product is an organic liquid with reduced oxygen content (approximately 10%), and the primary by-product is water containing soluble organic compounds.

The importance of the provisions for the supply of feedstocks as crops and other biomass are often underestimated since it is assumed that the supplies are inexhaustible. While this may be true over the long term, short-term supply of feedstocks can be as much as risk as any venture.

Anaerobic digestion is a natural process and is the microbiological conversion of organic matter to methane in the absence of oxygen. The decomposition is caused by natural bacterial action in various stages and occurs in a variety of natural anaerobic environments, including water sediment, water-logged soils, natural hot springs, ocean thermal vents, and the stomach of various animals (e.g., cows). The digested organic matter resulting from the anaerobic digestion process is usually called digestate.

Symbiotic groups of bacteria perform different functions at different stages of the digestion process. There are four basic types of microorganisms involved. Hydrolytic bacteria break down complex organic wastes into sugars and amino acids. Fermentative bacteria then convert those products into organic acids. Acidogenic microorganisms convert the acids into hydrogen, carbon dioxide, and acetate. Finally, the methanogenic bacteria produce biogas from acetic acid, hydrogen, and carbon dioxide.

The process of anaerobic digestion occurs in a sequence of stages involving distinct types of bacteria. Hydrolytic and fermentative bacteria first break down the carbohydrates, proteins and fats present in biomass feedstock into fatty acids, alcohol, carbon dioxide, hydrogen, ammonia, and sulfides. This stage is called hydrolysis (or liquefaction).

Next, acetogenic (acid-forming) bacteria further digest the products of hydrolysis into acetic acid, hydrogen, and carbon dioxide. Methanogenic (methane-forming) bacteria then convert these products into biogas.

The combustion of digester gas can supply useful energy in the form of hot air, hot water, or steam. After filtering and drying, digester gas is suitable as fuel for an internal combustion engine, which, combined with a generator, can

produce electricity. Future applications of digester gas may include electric power production from gas turbines or fuel cells. Digester gas can substitute for natural gas or propane in space heaters, refrigeration equipment, cooking stoves, or other equipment. Compressed digester gas can be used as a renewable transportation fuel.

Digestion can be either wet or dry. Dry digestion refers to mixtures which have a solid content of 30% or greater, whereas wet digestion refers to mixtures of 15% or less.

In recent years, increasing awareness that anaerobic digesters can help control the disposal and odor of animal waste has stimulated renewed interest in the technology. New digesters now are being built because they effectively eliminate the environmental hazards of dairy farms and other animal feedlots.

Anaerobic digester systems can reduce fecal coliform bacteria in manure by more than 99%, virtually eliminating a major source of water pollution. Separation of the solids during the digester process removes approximately 25% of the nutrients from manure, and the solids can be sold out of the drainage basin where nutrient loading may be a problem. In addition, the digester's ability to produce and capture methane from the manure reduces the amount of methane that otherwise would enter the atmosphere. Scientists have targeted methane gas in the atmosphere as a contributor to global climate change.

Controlled anaerobic digestion requires an airtight chamber, called a digester. To promote bacterial activity, the digester must maintain a temperature of at least 20°C (68°F). Using higher temperatures, up to 65°C (150°F), shortens processing time and reduces the required volume of the tank by 25% to 40%. However, there are more species of anaerobic bacteria that thrive in the temperature range of a standard design (mesophilic bacteria) than there are species that thrive at higher temperatures (thermophilic bacteria). High-temperature digesters also are more prone to upset because of temperature fluctuations, and their successful operation requires close monitoring and diligent maintenance.

The biogas produced in a digester (digester gas) is actually a mixture of gases, with methane and carbon dioxide making up more than 90% of the total. Biogas typically contains smaller amounts of hydrogen sulfide, nitrogen, hydrogen, methyl mercaptans, and oxygen. Methane is a combustible gas. The energy content of digester gas depends on the amount of methane it contains. Methane content varies from approximately 55% to 80%. Typical digester gas, with a methane concentration of 65%, contains approximately 600 Btu of energy per cubic foot.

There are three basic digester designs, and all of them can trap methane and reduce fecal coliform bacteria, but they differ in cost, climate suitability, and the concentration of manure solids they can digest.

A covered lagoon digester, as the name suggests, consists of a manure storage lagoon with a cover. The cover traps gas produced during decomposition of the manure. This type of digester is the least expensive of the three.

Covering a manure storage lagoon is a simple form of digester technology suitable for liquid manure with less than 3% solids. For this type of digester, an impermeable floating cover of industrial fabric covers all or part of the lagoon. A concrete footing along the edge of the lagoon holds the cover in place with an airtight seal. Methane produced in the lagoon collects under the cover. A suction pipe extracts the gas for use. Covered lagoon digesters require large lagoon volumes and a warm climate. Covered lagoons have low capital cost, but these systems are not suitable for locations in cooler climates or locations where a high water table exists.

A complete mix digester converts organic waste to biogas in a heated tank above or below ground. A mechanical or gas mixer keeps the solids in suspension. Complete mix digesters are expensive to construct and cost more than plug-flow digesters to operate and maintain.

Complete mix digesters are suitable for larger manure volumes having solids concentration of 3% to 10%. The reactor is a circular steel or poured concrete container. During the digestion process, the manure slurry is continuously mixed to keep the solids in suspension. Biogas accumulates at the top of the digester. The biogas can be used as fuel for an engine-generator to produce electricity or as boiler fuel to produce steam. Using waste heat from the engine or boiler to warm the slurry in the digester reduces retention time to less than 20 days.

Plug-flow digesters are suitable for ruminant animal manure that has a solids concentration of 11% to 13%. A typical design for a plug-flow system includes a manure collection system, a mixing pit, and the digester itself. In the mixing pit, the addition of water adjusts the proportion of solids in the manure slurry to the optimal consistency. The digester is a long, rectangular container, usually built below-grade, with an airtight, expandable cover.

New material added to the tank at one end pushes older material to the opposite end. Coarse solids in ruminant manure form a viscous material as they are digested, limiting solids separation in the digester tank. As a result, the material flows through the tank in a plug. The average retention time (the time a manure plug remains in the digester) is 20 to 30 days. Anaerobic digestion of the manure slurry releases biogas as the material flows through the

digester. A flexible, impermeable cover on the digester traps the gas. Pipes beneath the cover carry the biogas from the digester to an engine-generator set.

A plug-flow digester requires minimal maintenance. Waste heat from the engine-generator can be used to heat the digester. Inside the digester, suspended heating pipes allow hot water to circulate. The hot water heats the digester to keep the slurry at 25°C to 40°C (77°F to 104°F), a temperature range suitable for methane-producing bacteria. The hot water can come from recovered waste heat from an engine generator fueled with digester gas or from burning digester gas directly in a boiler.

See also: Aerobic Digestion, Anaerobic Digestion, Digesters.

Energy Production from Wood

Combustion remains the most common way of converting biomass into energy. It is well understood, relatively straightforward and commercially available, and can be regarded as a proven technology. However, the desire to burn uncommon fuels, improve efficiencies, cut costs, and decrease emission levels results in new technologies being continuously developed.

On the other hand, wood as a feedstock for storing solar energy, is a renewable energy source. It is a relatively clean, efficient, safe energy source having low sulfur content and is generally found throughout the country. Its primary products of combustion are carbon dioxide, water vapor, and ash. The ash content is low (typically 1-2% w/w) and that which does remain can be used as a worthwhile soil conditioner.

A wood fire is easy to start and produces a large quantity of heat in a short time as well as adding a cheerful atmosphere to the home. An ample air supply to the wood fire is important to ensure complete burning of combustible gases. Wood fires are ideal where heat is required only occasionally, for warming a living area on cool days or for supplying extra heat in extremely cold weather. When considering wood as a primary heat source, several factors must be carefully weighed to ensure satisfactory results and acceptable deficiencies.

Generally, hardwoods which provide long-burning fires contain the greatest total heating value per unit of volume. Softwoods which give a fast-burning, cracking blaze are less dense and contain less total heating value per unit of volume. However, the amount and types of wood fuel used vary considerably between regions, mainly due to different local situations and conditions.

Charcoal continues to be used as an important industrial source of energy for use in heavy industry, such as steel and alloy production. The industrial demand for charcoal in the last few years has led to new, more efficient and large-scale technologies, mainly aimed at improving charcoal yield and quality.

On the other hand, the production and consumption of black liquor, which is a by-product of pulp and paper production, are concentrated in developed countries with large paper industries. In the pulp and paper industry, black liquors are widely used for heat and power production. Almost all of the energy needs for industry are met by black liquors, with surplus electricity being sold to the public grid in some cases. A combination of factors such as higher oil prices and technological developments in wood fuel production, transportation, and combustion is also making wood fuels more attractive.

Combustion remains the most common way of converting biomass into energy. It is well understood, relatively straightforward and commercially available, and can be regarded as a proven technology. However, the desire to burn uncommon fuels, improve efficiencies, cut costs, and decrease emission levels results in new technologies being continuously developed.

Some industry associations are also making special voluntary contributions to reduce the consumption of fossil fuels and increase the use of wood-based energy. For instance, the European paper industry aims to achieve an approximately 25% increase in the amount of wood fuel used for on-site heat and power production by 2010, and increase the share of wood in its on-site total primary energy consumption from 49 to 56%.

The development of sustainable wood energy systems remains one of the most critical issues to be addressed by policy makers and community planners. With society giving increasing attention to sustainability issues, in the case of wood energy in both developing and developed countries, economic, environmental, and social issues deserve particular attention. Most of the uses of wood are accounted for by combustion in intermediate or large-scale units outside the forest industries (e.g., in schools, hospitals, barracks, or district heating plants), with minor volumes

going to the production of charcoal. Small volumes were used in a few European countries to generate electricity or to manufacture solid fuels (e.g., briquettes).

Wood is used as a source of energy in a number of forms, and although the generation of electricity from wood is growing, the outlook is less clear for the new types of wood-derived energy that include gaseous fuels (often seen as substitutes or additives to traditional fuels).

See also: Energy from Crops.

Energy Sources

Energy sources are those natural-occurring material that can be used to produce energy. The prime sources of energy have been the various sources known as fossil fuels which are natural gas, crude oil, and coal (Table E-3). Enormous resources of other fossil fuels exist, but they are not yet in large-scale commercial use. Examples of fossil fuels not used currently, but potentially useful in the future, are oil shale and (with the exception of commercialization in Alberta, Canada) tar sand deposits (Table E-3).

Table E-3 General sub-divisions of energy sources.

<i>Conventional Energy Sources</i>
Natural Gas
Crude oil
Heavy Crude Oil
Coal*
<i>Non-conventional Energy Sources</i>
Extra Heavy Crude Oil
Tar sand Bitumen
Coal*
Coal Gas
Coal Liquids
Shale Oil
<i>Renewable Energy Sources</i>
Biomass
Hydrogen
Hydroelectric**
Nuclear
Solar Energy
Ocean Energy**
Tidal Energy**
Wind Energy

*When used as a solid fuel feedstock for combustion (without any modification other than cleaning), coal is often considered to be a conventional energy source.

**Often grouped together under the name “hydrokinetic energy” – hydroelectric energy may also be included in this group.

Over the past 20 to 30 years, the use of older renewable energy sources has increased and there has been a start to the use of new renewable energy sources as well. There has been the realization that fossil fuels and atomic fuels will not last forever, and that the use of these fuel sources and the fuels contributes to environmental pollution.

Renewable energy – which basically comes from the sun in one way or another – provides opportunities for an unlimited, sustainable energy supply with low environmental impact. And renewable energy is not just something for the future, but something that can be used in homes.

True renewable energy sources are energy supplies that are refilled by natural processes at least as fast that can be used. All renewable energy comes, ultimately, from the Sun. The Sun can be used directly (as in solar heating systems) or indirectly (as in hydroelectric power, wind power, and power from biomass fuels). Renewable energy supplies can become exhausted if they are used faster than they become replenished: most of England's forests were cut down for fuel before the English started using coal. If used wisely, however, renewable energy supplies can last forever. There are other alternatives to the typical energy sources that are not renewable. Although these are alternative energy sources rather than renewable energy sources, they use the energy more efficiently than older technologies. In doing this, they help to make the existing energy supplies last longer and give more time before the stored fossil and atomic fuels are completely depleted. Listed below are brief descriptions of these resources.

Biomass

Biomass is second to hydropower as a leader in renewable energy production. Biomass has an existing capacity of over 7,000 MW. Biomass as a fuel consists of organic matter such as industrial waste, agricultural waste, wood, and bark. Biomass can be burned directly in specially designed power plants, or used to replace up to 15% of coal as a fuel in ordinary power plants. Biomass burns cleaner than coal because it has less sulfur, which means less sulfur dioxide will be emitted into the atmosphere. Biomass can also be used indirectly since it produces methane gas as it decays or through a modern process called gasification. Methane can produce power by burning in a boiler to create steam to drive steam turbines or through internal combustion in gas turbines and reciprocating engines. The largest use of biomass energy in Virginia is the forest products industry. Furniture plants, sawmills, and paper mills usually burn their wood waste to produce heat and electricity. Many homeowners use firewood or pellets for winter heat.

Geothermal Energy

Geothermal electric capacity in the United States is over 3,000 MW. Geothermal power plants use high temperatures deep underground to produce steam, which then powers turbines that produce electricity. Geothermal power plants can draw from underground reservoirs of hot water or can heat water by pumping it into hot, dry rock. High underground temperatures are accessed by drilling wells, sometimes more than a mile deep. In one sense, this geothermal energy is not renewable, since sometime in the future the core of the earth will cool. That time is so far off (hundreds of millions of years) that we think of it as renewable. Most geothermal power plants are located in the western United States, but some coastal regions of the eastern United States have geothermal power potential. Geothermal heat pumps use compressors to pump heat out of the earth (for winter heating) or into the earth (when running as air conditioners in summer). The energy they pump into and out of the earth is renewable since it is replaced by the cycle of the seasons. The energy that runs the compressor can either be renewable or conventional.

Hydropower

Hydropower represents one of the oldest and largest renewable powers. Hydropower plants convert the energy of flowing water into electricity. This is primarily done by damming rivers to create large reservoirs and then releasing water through turbines to produce electricity. Hydropower results in no emissions into the atmosphere, but the process of damming a river can create significant ecological problems for water quality and for fish and wildlife habitat.

Solar Energy

Solar energy comes directly from the power of the sun and is used to produce electricity, to produce heat, and for light. Solar represents a small share of the electric market in the United States – approximately one-half of 1% of electrical capacity. Solar's contribution to heating and lighting is much larger. Solar-electric power can be produced, either by power plants using the sun's heat or by photovoltaic (PV) technology, which converts sunlight directly to electricity using solar cells. PV technology is more practical for residential use. Systems to use the heat of the sun

directly can be either active or passive. In active systems, air or liquid circulates through solar collectors and bring heat to where it is used. In passive systems, buildings are built with windows and heat-absorbing surfaces set up to maximize solar heating in winter. Either technology is suitable for residential use. Systems to directly use the light of the sun are most common. The most usual device for using sunlight is the window, but skylights and skylight tubes are also used.

Wind Power

Wind energy represents 4,700 megawatts (MW) of installed electric capacity in the United States. Wind has been the fastest-growing energy source in the U.S. over the last decade mainly due to significant improvements in wind energy technology. The American Wind Energy Association predicts that 6,000 MW of wind power will be installed by the end of 2004. This is enough to power 1.5 million homes. Wind power is produced by the energy of the wind turning aerodynamic blades mounted to a hub. The hub is connected to a shaft that turns a generator. Large utility-scale wind turbines range in size from 50 kilowatts to over four megawatts. Smaller wind towers (under 50 kW) are suitable for residential and agricultural use.

Enersludge Process

The Enersludge process is an alternative to incineration or anaerobic digestion of sewage sludge (or dumping it out at sea, which is still often used as the disposal method which converts the sludge into useful bio-oil).

In essence, this plant uses standard technology, which is fairly common in Europe, to produce dry pellets from the raw sludge. The pellets have a fertilizer and soil conditioning value and are free of pathogens, etc. The innovative part of the Enersludge process is the addition of a pyrolysis unit, which produces gas, char, and oil. The gas and char are used to heat the plant, leaving the bio-oil for revenue-earning activities - either for direct sale or for use on site in an internal combustion engine to produce electricity and offset purchases.

In the process, after being macerated, the raw primary sludge is mixed with active sludge that is in excess when being circulated through the treatment plant so it is taken off and thickened by air diffusion. The blend then leaves the mixer tanks and enters the dewatering centrifuges. Polymers are added to help settle out the solids and results in a sticky cake material. The dilute fraction is separated and returned to the treatment plant and then eventually discharged out to sea.

The alternative option is for the cake to enter the rotary dryer, which is approximately 6 feet in diameter and 20 feet long. An LPG burner is installed as a back-up system for the dryer. The pellets are graded by size using a shaker table - returning the too large and too fine portions for reprocessing through the dryer. The bulk density of the pellets is the quality control measurement, and only after several modifications, including a means of removing hair from the system, was it proved successful.

The Enersludge process converts these pellets into fuel, some of which is used for drying heat. Normally, the pellets are conveyed from the dryer direct to the pyrolysis conversion reactor, although when this is being maintained, up to 50% can be used for fuel in the hot gas generator and the remaining fraction is then sold or dumped. The pyrolysis process involves two stages, with volatiles being driven off at the first stage and the char passing from stage 1 to stage 2. The heavy metals present in the sludge act as catalysts. An LPG burner is installed to maintain the temperature at 400°C. From 1 ton of pellets, around 80 gallons of bio-oil is produced. In the longer term, it is hoped to produce this bio-oil to a sufficient standard in order to provide a portion of the power requirements for the site.

The hot gas generator is a fluidized bed incinerator designed originally for burning coal dust, but scaled down. Ash from the fluidized bed incinerator includes the heavy metals that are now immobilized. This can either be land-filled or used in a concrete mix to make terracotta paving bricks.

Enrichment

The purpose of enrichment is to produce a gas stream for sale and enriched tank oil. The tank oil contains more low-boiling hydrocarbon liquids than natural crude oil, and the residue gas is drier (leaner, i.e., has lesser amounts

of the higher-molecular-weight hydrocarbon derivatives). Therefore, the process concept is essentially the separation of hydrocarbon liquids from the methane to produce a lean, dry gas.

Crude oil enrichment is used when there is no separate market for low-boiling hydrocarbon liquids or when the increase in API gravity of the crude provides a substantial increase in the price per unit volume as well as volume of the stock tank oil. A very convenient method of enrichment involves manipulation of the number and operating pressures of the gas-oil separators (traps). However, it must be recognized that alteration or manipulation of the separator pressure affects the gas compression operation as well as influences other processing steps.

One method of removing light ends involves the use of a pressure reduction (vacuum) system. Generally, stripping of light ends is achieved at low pressure, after which the pressure of the stripped crude oil is elevated so that the oil acts as an absorbent. The crude oil, which becomes enriched by this procedure, is then reduced to atmospheric pressure in stages or using fractionation (rectification).

See also: Gas Cleaning, Gas Processing, Gas Treating.

Entrained-Bed Combustion

In entrained-bed combustion systems, fine grinding and increased retention times intensify combustion but the temperature of the carrier and degree of dispersion are also important. In practice, the coal is introduced at high velocities which may be greater than 100 feet/second and involve expansion from a jet to the combustion chamber. The pulverized coal is usually suspended in a stream of primary air (approximately 25% of the total air requirement), and the remainder of the air for combustion is introduced as secondary air. The secondary air may be introduced at an inlet region surrounding, or adjacent to, the primary air duct. The temperature of the primary air should be regulated within limits; a temperature of at least 60°C (140°F) is required to prevent the condensation of moisture in the lines, but at temperatures of 80 to 130°C (175 to 265°F) bituminous coal particles, for instance, will soften and stick.

See also: Combustion.

Entrained-Bed Gasifier

In the entrained bed (entrained flow) gasifier, a dry pulverized solid, an atomized liquid fuel, or a fuel slurry is gasified with oxygen (much less frequent: air) in co-current flow. The gasification reactions take place in a dense cloud of fine particles. Most coal is suitable for this type of gasifier because of the high operating temperatures and because the coal particles are well separated from one another. The high temperatures and pressures also mean that a higher throughput can be achieved, but thermal efficiency is somewhat lower as the gas must be cooled before it can be cleaned with existing technology. The high temperatures also mean that tar and methane are not present in the product gas; however, the oxygen requirement is higher than for the other types of gasifiers. All entrained flow gasifiers remove the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a fine dry fly ash or as black fly ash slurry. Some fuels, in particular certain types of biomasses, can form slag that is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. However, some entrained bed type of gasifiers do not possess a ceramic inner wall but have an inner water or steam cooled wall covered with partially solidified slag. These types of gasifiers do not suffer from corrosive slag. Some fuels have ashes with a high ash fusion temperature. In this case, mostly limestone is mixed with the fuel prior to gasification. Addition of limestone will usually suffice for lowering the fusion temperatures. The fuel particles must be much smaller than for other types of gasifiers. This means the fuel must be pulverized, which requires somewhat more energy than for the other types of gasifiers. By far, the most energy consumption related to entrained bed gasification is not the milling of the fuel but the production of oxygen used for the gasification.

Thus, in the entrained flow gasifier, a dry pulverized solid, an atomized liquid fuel, or a fuel slurry is gasified with oxygen (much less frequent: air) in co-current flow. The gasification reactions take place in a dense cloud of fine particles. Most coals are suitable for this type of gasifier because of the high operating temperatures and because the coal particles are well separated from one another. The high temperatures and pressures also mean that a higher throughput can be achieved; however, thermal efficiency is somewhat lower as the gas must be cooled before it can

be cleaned with existing technology. The high temperatures also mean that tar and methane are not present in the product gas; however, the oxygen requirement is higher than for the other types of gasifiers. All entrained flow gasifiers remove the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a fine dry fly ash or as a black colored fly ash slurry. Some fuels, in particular certain types of biomasses, can form slag that is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. However, some entrained bed type of gasifiers do not possess a ceramic inner wall but have an inner water or steam cooled wall covered with partially solidified slag.

See also: Entrained-Bed, Gasification, Gasifiers.

Entrained-Flow Process

The process is based on an air-blown, atmospheric pressure, entrained-bed slagging gasifier, and in the process, part of the coal char is charged to the combustion section of the gasifier to supply the heat necessary for the endothermic gasification reaction.

In the combustion section, substantially all of the ash in the system is converted to molten slag, which is removed via the bottom of the gasifier. The remainder of the coal is fed to the reaction section of the gasifier where it is contacted with hot gases entering the reaction zone from the combustor. The gasification process takes place in the entrainment section of the reactor where the coal is devolatilized and reacts with the hot gases to produce the desired product gas.

The gas contains solid particles and hydrogen sulfide; the former are removed and recycled to the combustor by means of a spray drier, cyclone separators, and venturi scrubbers, and the hydrogen sulfide is removed and elemental sulfur produced by the Stretford process.

See also: Entrained-Bed, Entrained-Bed Combustion, Entrained-Bed Reactor.

Entrained Flow Reactor

This type of reactor is also referred to as entrained flow reactor since there is no bed of solids in the most practical sense. This reactor system uses finely pulverized coal particles blown into the gas stream before entry into the reactor, with combustion and gasification occurring inside of the coal particles suspended in the gas phase. Due to the entrainment requirement, high space velocity of gas stream and fine powdery coal particles are very essential to the operation of this type of process. Due to the short residence time (i.e., high space velocity) in the reactor, a high temperature is required to achieve a good conversion in such a short period of reaction time. This can also be assisted by using excess oxygen. This bed configuration is typically capable of handling both caking and non-caking coals without much operational difficulty. Examples of commercial gasifiers that use this type of reactor include Koppers-Totzek gasifier and Texaco gasifier.

See also: Entrained Bed Gasifier.

Environment

The environment is the sum of all external factors (biotic and abiotic) that influence the life of an organism. Biotic factors include all living beings (for example, humans, animals, plants, and microorganisms), whereas abiotic factors include all physico-chemical entities (such as air, water, soil, rocks, minerals, and mountains). The environment can be natural, human engineered, or even abstract (non-material). Owing to such vagueness, the term environment has been used in various ways or in various perspectives. For example, terms such as natural environment, extra-terrestrial environment, human-engineered environment, socio-political-cultural environment, business environment, family environment, and workplace environment are used in general conversation.

The influence of the environment on organisms can be viewed on a large scale (i.e., the relationship between regional climate and geographic distribution of organisms) or on a smaller scale (i.e., some highly localized conditions determine the precise location and activity of individual organisms). For example, an organisms may respond

differently to the frequency and duration of a given environmental change. In addition, if some individual organisms in a population have adaptations which allow them to survive and to reproduce under new environmental conditions, the population will continue but the genetic composition will have changed (Darwinism). On the other hand, some organisms have the ability to adapt to the environment (i.e., to adjust their physiology or morphology in response to the immediate environment) so that the new environmental conditions are less (certainly no more) stressful than the previous conditions. But such changes may not be genetic (Lamarckism).

Environmental Ethics

Environmental ethics involves the study of the moral relationship of human beings with the environment and its non-human contents. This is especially important to scientists and engineers who are working on issues related to maintaining an environment that is as close as possible to a pristine environment. Thus, environmental ethics is the part of environmental philosophy which considers extending the traditional boundaries of ethics from solely including humans to including the nonhuman world. It exerts influence on a large range of disciplines including law, sociology, theology, economics, ecology, and geography. Environmental ethics ensures that humans should base their behavior on a set of ethical values that guide the human approach toward the other living beings in nature. Even if the human race is considered the primary concern of society, plants and animals (flora and fauna) are also important have the right of existence.

The concept of environmental ethics developed into a specific philosophical discipline in the 1970s due to the increasing awareness in the 1960s of the effects that technology, industry, economic expansion, and population growth were having on the environment. However, pollution and the depletion of natural resources have not been the only environmental concerns since that time and issues such as (i) dwindling plant and animal biodiversity, (ii) the loss of wilderness areas, (iii) the degradation of ecosystems, and (iv) climate change are all part of a raft of issues that have implanted themselves into both public consciousness and public policy over subsequent years.

Thus, environmental ethics deals with the issues related to the rights and duties of individuals that are fundamental to the life and well-being of present human society, future generations (of humans), as well as of other living beings present on the Earth. Environmental ethics evolved in the 1970s as a sub-discipline of environmental science and environmental engineering. The subject differs from traditional ethics which is concerned with relationships among humans only. The need of environmental ethics has arisen as a result of the following three major factors: (i) modern technological civilization has been affecting nature greatly; therefore, there is a need to analyze the consequences of human actions, (ii) as a result of the advancement of science, human understanding related to nature and environmental problems is increasing, and (iii) there is a concern – or belief – that other living species have equal rights to live on the Earth is also raising the need for environmental ethics. Therefore, it is necessary to understand and accept that the life-supporting environment of the Earth is the outcome of complex interaction of innumerable physical, chemical, and biological factors. With the advancement in the methods of scientific investigation, the human understanding of these factors is also increasing.

The term conservation ethics is an extension of use-value in _____ to the non-human biological world which focuses only on the worth of the environment in terms of its utility or usefulness to humans. The concept generally advocates preservation of the environment on the basis that it has extrinsic value insofar as it is instrumental to the welfare of human beings. Conservation is therefore a means to an end and purely concerned with mankind and inter-generational considerations.

Conservation ethics is related to anthropocentrism which advocates that humans are the most important or critical element in any given situation; that the human race must always be its own primary concern.

See also: Environmental Issues, Sustainability.

Environmental Issues

There are two areas of environmental concern when considering using biomass as a form of energy. First, there is the issue of land degradation and deforestation – this concern can be addressed by proper management of sustainable

energy crops. Although much of the biomass requirement for energy production can be met through utilizing residues from the food industry, from agriculture, or from commercial activity, careful planning of energy cropping is required to prevent undue stress on the environment.

With the recent global call to reduce carbon dioxide emissions, there is a strong case for promoting the use of sustainable biomass-to-energy technologies worldwide. Using modern technology, enormous reductions can be made in carbon dioxide emissions, particularly if liquid biofuels are used to replace their fossil-based equivalents. In fact, if biomass energy production is done on a sustainable basis, there is little net carbon dioxide addition to the environment. There are other environmental concerns related to each fuel that need to be kept in mind, such as toxic emissions and production of tar and soot.

There is a consensus among scientists that biomass fuels used in a sustainable manner result in no net increase in atmospheric carbon dioxide (CO_2). Some would even go as far as to declare that sustainable use of biomass will result in a net decrease in atmospheric CO_2 . This is based on the assumption that all the CO_2 given off by the use of biomass fuels was recently taken in from the atmosphere by photosynthesis. Increased substitution of fossil fuels with biomass-based fuels would therefore help reduce the potential for global warming, caused by increased atmospheric concentrations of carbon dioxide.

Unfortunately, things may not be as simple as has been assumed above. Currently, biomass is being used all over the world in a very unsustainable manner, and the long-term effects of biomass energy plantations have not been proven. As well, the natural humus and dead organic matter in the forest soils is a large reservoir of carbon. Conversion of natural ecosystems to managed energy plantations could result in a release of carbon from the soil as a result of the accelerated decay of organic matter.

An ever-increasing number of people on this planet are faced with hunger and starvation. It has been argued that the use of land to grow fuel crops will increase this problem. Hunger in developing countries, however, is more complex than just a lack of agricultural land. Many countries in the world today, such as the U.S., have food surpluses. Much fertile agricultural land is also used to grow tobacco, flowers, food for domestic pets, and other "luxury" items, rather than staple foods. Similarly, a significant proportion of agricultural land is used to grow feed for animals to support the highly wasteful, meat-centered diet of the industrialized world. By feeding grain to livestock, the result is approximately 10% of the caloric content of the grain. When looked at in this light, it does not seem to be so unreasonable to use some fertile land to grow fuel. Marginal land and underutilized agricultural land can also be used to grow biomass for fuel.

Acid rain, which can damage lakes and forests, is a by-product of the combustion of fossil fuels, particularly coal and oil. The high sulfur content of these fuels together with hot combustion temperatures result in the formation of sulfur dioxide (SO_2) and nitrous oxides (NO_x) when they are burned to provide energy. The replacement of fossil fuels with biomass can reduce the potential for acid rain. Biomass generally contains less than 0.1% sulfur by weight compared to low sulfur coal with 0.5–4% sulfur. Lower combustion temperatures and pollution control devices such as wet scrubbers and electro-static precipitators can also keep emissions of NO_x to a minimum when biomass is burned to produce energy.

The final major environmental impact of biomass energy may be that of loss of biodiversity. Transforming natural ecosystems into energy plantations with a small number of crops, as few as one, can drastically reduce the biodiversity of a region. Such "monocultures" lack the balance achieved by a diverse ecosystem, and are susceptible to widespread damage by pests or disease.

Biomass is by no means the only solution to global warming and other problems, and the environmental effects of its use should be examined very closely.

For instance, the combustion of wastes solves a disposal problem and may offset the use of fossil fuels but the incombustible materials such as ash have to be removed from the site. This incurs a cost to the environment due to pollution from transportation. In addition, if care is not taken and a conventional combustion chamber is used (as opposed to a newly designed one that is capable of filtering out harmful emissions), by-products such as particulates and poly-aromatic hydrocarbon derivatives (PAHs) can escape to the atmosphere.

On the other hand, tree planting on a large scale (such as the one needed for arable coppicing) helps in the absorption of CO_2 . If care is taken in the overall processing (harvesting, chipping, transporting, drying, and so on) of this biomass feedstock, then the net carbon dioxide emissions after it has been used for fuel will be less than the absorbed carbon dioxide, thus benefiting the environment.

On the other hand, methane is a very harmful greenhouse gas as well as causing accidental explosions due to its migration from landfill sites to nearby buildings. Moreover, it has 30 times the damaging effect on the environment

than that of CO_2 . The extraction, use of, and combustion of methane actually protects against global warming. Even though a by-product of the process is carbon dioxide, the net effect to the environment is much smaller.

Finally, another issue concerning the environment is the use of set-aside land for energy crops. SRC has potential as there are only a few stumbling points that may cause some objections; for example, the potentially sensitive nature of sites has to be considered – proximity to settlements and roads – as views could be impeded due to the growth rates causing a 3-dimensional woodland type mass in the field. But integrating the area with the surrounding landscape – trees and other features – when establishing new plantations can reduce visual impact. Also, changes in the landscape can be quick during growth and also during harvesting.

Additionally, the scale of short rotation coppicing has to be considered to avoid saturation of the landscape by monotonous planting. F farming conforms with regulations related to adjacent plots of different tree species and so, on most of the above concerns, can turn out to be unfounded.

See also: Environmental Ethics, Environmental Issues – Biomass Use.

Environmental Issues – Biomass Use

There are two areas of environmental concern when considering using biomass as a form of energy. Firstly, there is the issue of land degradation and deforestation. This concern can be addressed by proper management of sustainable energy crops. Although much of the biomass requirement for energy production can be met through utilizing residues from the food industry, from agriculture, or from commercial activity, careful planning of energy cropping is required to prevent undue stress on the environment.

With the recent global call to reduce carbon dioxide emissions, there is a strong case for promoting the use of sustainable biomass-to-energy technologies worldwide. Using modern technology, enormous reductions can be made in carbon dioxide emissions, particularly if liquid biofuels are used to replace their fossil-based equivalents. In fact, if biomass energy production is done on a sustainable basis, there is little net carbon dioxide addition to the environment.

There are other environmental concerns related to each fuel that need to be kept in mind, such as toxic emissions and production of tar and soot.

There is a consensus among scientists that biomass fuels used in a sustainable manner result in no net increase in atmospheric carbon dioxide (CO_2). Some would even go as far as to declare that sustainable use of biomass will result in a net decrease in atmospheric carbon dioxide. This is based on the assumption that all of the carbon dioxide that is emitted by the use of biomass fuels was recently taken in from the atmosphere by photosynthesis. Increased substitution of fossil fuels with biomass-based fuels would therefore help reduce the potential for global warming, caused by increased atmospheric concentrations of carbon dioxide.

Unfortunately, things may not be as simple as has been assumed above. Currently, biomass is being used all over the world in a very unsustainable manner, and the long-term effects of biomass energy plantations have not been proven. As well, the natural humus and dead organic matter in the forest soils are a large reservoir of carbon. Conversion of natural ecosystems to managed energy plantations could result in a release of carbon from the soil as a result of the accelerated decay of organic matter.

An ever-increasing number of people on this planet are faced with hunger and starvation. It has been argued that the use of land to grow fuel crops will increase this problem. Hunger in developing countries, however, is more complex than just a lack of agricultural land. Many countries in the world have food surpluses. Much fertile agricultural land is also used to grow tobacco, flowers, food for domestic pets, and other “luxury” items, rather than staple foods. Similarly, a significant proportion of agricultural land is used to grow feed for animals to support the highly wasteful, meat-centered diet of the industrialized world. By feeding grain to livestock, there is only approximately 10% of the caloric content of the grain. When looked at in this light, it does not seem to be so unreasonable to use some fertile land to grow fuel. Marginal land and underutilized agricultural land can also be used to grow biomass for fuel.

Acid rain, which can damage lakes and forests, is a by-product of the combustion of fossil fuels, particularly coal and oil. The high sulfur content of these fuels together with hot combustion temperatures result in the formation of sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) when they are burned to provide energy. The replacement of fossil fuels with biomass can reduce the potential for acid rain. Biomass generally contains less than 0.1% sulfur by weight

compared to low sulfur coal with 0.5-4% sulfur. Lower combustion temperatures and pollution control devices such as wet scrubbers and electro-static precipitators can also keep the emissions of oxides of nitrogen to a minimum when biomass is burned to produce energy.

The final major environmental impact of biomass energy may be that of loss of biodiversity. Transforming natural ecosystems into energy plantations with a small number of crops, as few as one, can drastically reduce the biodiversity of a region. Such “monocultures” lack the balance achieved by a diverse ecosystem, and are susceptible to widespread damage by pests or disease.

Biomass is by no means the only solution to global warming and other problems, and the environmental effects of its use should be examined very closely.

For instance, the combustion of wastes solves a disposal problem and may offset the use of fossil fuels, but the incombustible materials such as ash have to be removed from the site. This incurs a cost to the environment due to pollution from transportation. In addition, if care is not taken and a conventional combustion chamber is used (as opposed to a newly designed one that is capable of filtering out harmful emissions), by-products such as particulates and poly-aromatic hydrocarbon derivatives (PAHs, also called polynuclear aromatic hydrocarbon derivatives, PNAs) can escape to the atmosphere.

On the other hand, tree planting on a large scale (such as the one needed for arable coppicing) helps in the absorption of carbon dioxide. If care is taken in the overall processing (harvesting, chipping, transporting, drying, and so on) of this biomass feedstock, then the net carbon dioxide emissions after it has been used for fuel will be less than the absorbed carbon dioxide thus benefiting the environment.

On the other hand, methane is a very harmful greenhouse gas as well as causing accidental explosions due to its migration from landfill sites to nearby buildings. Moreover, it has 30 times the damaging effect on the environment than that of carbon dioxide. The extraction, use of, and combustion of methane actually protects against global warming. Even though a by-product of the process is carbon dioxide, the net effect to the environment is much smaller.

Finally, another issue concerning the environment is the use of set-aside land for energy crops. SRC has potential as there are only a few stumbling points that may cause some objections; for example, the potentially sensitive nature of sites has to be considered – proximity to settlements and roads – as views could be impeded due to the growth rates causing a 3-dimensional woodland-type mass in the field. But integrating the area with the surrounding landscape – trees and other features – when establishing new plantations can reduce visual impact. Also, changes in the landscape can be quick during growth and also during harvesting.

Additionally, the scale of short rotation coppicing has to be considered to avoid saturation of the landscape by monotonous planting. F farming conforms with regulations related to adjacent plots of different tree species and so, on most of the above concerns, can turn out to be unfounded.

Enzymatic Hydrolysis

Enzymatic hydrolysis is a process in which enzymes facilitate the cleavage of bonds in molecules with the addition of the elements of water and plays an important role in the human system for the digestion of food. In the current context, the process involves the addition of cellulases (a group of enzymes which, when acting together, hydrolyze cellulose) to hydrolyze pretreated lignocellulosic biomass into fermentable sugars. The process involves several key steps: (i) transfer of enzymes from the bulk aqueous phase to the surface of the cellulose, (ii) adsorption of the enzymes and formation of enzyme-substrate complexes, (iii) hydrolysis of the cellulose, (iv) transfer of the hydrolysis products from the surface of the cellulosic particles to the bulk aqueous phase, and (v) hydrolysis of the sugar-type products to glucose in the aqueous phase. The overall rate of the process is influenced by the structural features of lignocellulosic biomass and the composition and source of the cellulases.

Thus, the enzymatic hydrolysis process was developed to better utilize both cellulose and hemicellulose from lignocellulosic materials. The enzymatic process must be preceded by extensive pre-treatment to separate cellulose, hemicellulose, and lignin. Because milder conditions are used compared to acid hydrolysis of cellulose, subsequent enzymatic hydrolysis of the cellulose does not degrade pentoses during pre-hydrolysis. Cellulose is a homopolysaccharide of glucose linked by 1,4-glycoside-type bonds (bonds in which a sugar molecule is bound to another functional group, also known as glycosidic bond). Enzymatic hydrolysis of cellulose proceeds in several steps to break

glycoside-type bonds by the action of a system of enzymes known as cellulase. The system of enzymes also contains hemicellulase to hydrolyze any hemicellulose not solubilized by prehydrolysis. Unfortunately, enzymatic technologies are not likely to be suitable for unsorted municipal solid waste due to its high heterogeneity, and further research is necessary to convert wastes that are high in hemicellulose.

In a fermentation process, glucose is fermented to produce a dilute ethanol-water solution (dilute beer). Xylose is difficult to convert to ethanol, but it does occur. Lignin, which is not susceptible to biological transformation, can be chemically upgraded or more frequently, simply burned as boiler fuel.

Simultaneous saccharification and fermentation (SSF) has been developed for fermenting sugars released from lignocellulose. The process combines hydrolysis and fermentation to overcome end product inhibition. By combining hydrolysis and fermentation, glucose is rapidly removed before it can inhibit further hydrolysis. In the process, biomass feedstock is milled and then pre-hydrolyzed to yield a mixture of pentoses (xylose and arabinose) and fiber. The mixture is neutralized with limestone and mixed with cellulase and hemicellulase enzymes. The cellulose and any remaining hemicellulose are solubilized to hexose (glucose) and pentoses (xylose and arabinose), which are immediately fermented to ethanol. The optimum temperature for the hydrolysis-fermentation reaction is between the optimum temperature for cellulase activity and the best temperature for the yeast. Lignin is separated from the mixture and used as boiler fuel or converted to high-value octane enhancers that can be blended with gasoline.

The first application of enzymes to wood hydrolysis in an ethanol process was simply to replace the cellulose acid hydrolysis step with a cellulase enzyme hydrolysis step. This is called separate hydrolysis and fermentation. The most important process improvement made for the enzymatic hydrolysis of biomass was the introduction of simultaneous saccharification and fermentation (SSF) which reduced the number of reactors involved by eliminating the separate hydrolysis reactor and, more importantly, avoiding the problem of product inhibition associated with enzymes.

In the simultaneous saccharification and fermentation process, cellulase enzyme and fermenting microbes are combined. As sugars are produced by the enzymes, the fermentative organisms convert them to ethanol. The SSF process has recently been improved to include the co-fermentation of multiple sugar substrates.

Cellulase enzymes are already commercially available for a variety of applications. Most of these applications do not involve extensive hydrolysis of cellulose. For example, the textile industry applications for cellulases require less than 1% hydrolysis. Ethanol production, by contrast, requires nearly complete hydrolysis. In addition, most of the commercial applications for cellulase enzymes represent higher value markets than the fuel market. For these reasons, there is quite a large leap from the current cellulase enzyme industry to the fuel ethanol industry.

See also: Enzymes.

Enzymes

Enzymes (biocatalysts) are complex protein-based compounds produced by living cells, and they catalyze hydrolysis and oxidation reactions. With the current drive toward production of renewable fuels from plant material, enzymes which can break down this material into useable compounds are required in industrial quantities and at a low cost.

In addition to enhancing the reaction rate, enzymes have the ability to discriminate among competing substrates. Enzyme specificity arises mainly from three sources which are (i) the exclusion of other molecules from the active site because of the presence of incorrect functional groups, or the absence of necessary binding groups, (ii) many weak interactions exist between the substrate and the enzyme, and (iii) stereospecificity arises from the fact that enzymes are built from only L-amino acids and have active sites which are asymmetric and will bind only certain substrates.

Traditional methods of generating enzymes for biofuel production currently operate at over five times the target cost required to make the fuels financially competitive. By using plants which have been engineered to make the proteins, it may be possible to meet this target. One option is to focus on producing cellulase, enzymes which can break down biomass, such as the constituents of maize seed. By carefully designing the processing chain, from a single crop of maize, oil that can be turned into biodiesel can be produced.

Enzyme-based biofuel cells are attracting attention rapidly partially due to the promising advances reported recently. However, there are issues to be addressed before biofuel cells become competitive in practical applications. Two critical issues are short lifetime and poor power density, both of which are related to enzyme stability, electron transfer rate, and enzyme loading.

Enzymatic activity is regulated in four general ways, which are (i) allosteric control, which is due to allosteric enzymes – the enzymes that have distinct binding sites for effector molecules, which control their rates of reaction, (ii) designated control proteins, which participate in cellular regulatory processes, (iii) a mechanism involves the reversible chemical modification that can be carried out with a variety of chemical groups, and (iv) proteolytic activation, which involves activation of enzyme activity that occurs when part of the protein is removed) can regulate the activity of some enzymes. Proteolytic enzymes are controlled by this latter mechanism.

Also, enzyme inhibitors diminish the activity of an enzyme by altering the way substrates bind to the enzyme. The structure of the inhibitor may be similar to the substrate – chemically, an inhibitor may be a large organic molecule, or a small molecules, or an ion. Inhibitors work in either a reversible or an irreversible manner. Irreversible inhibition is characterized by interaction of the inhibitor with the enzyme, resulting in slow dissociation and inactivation. There are three main classes of reversible inhibition, which are (i) competitive inhibition, (ii) noncompetitive inhibition, and (iii) mixed inhibition which are distinguishable by the manner in which the inhibitor binds to the enzyme and the response to increasing substrate concentration.

Recent progress in nano-biocatalysis opens the possibility to improve in these aspects. Many nano-structured materials, such as mesoporous media, nanoparticles, nanofibers, and nanotubes, have been demonstrated as efficient hosts of enzyme immobilization. It is evident that, when nanostructure of conductive materials are used, the large surface area of these nanomaterials can increase the enzyme loading and facilitate reaction kinetics, and thus improving the power density of biofuel cells. In addition, research efforts have also been made to improve the activity and stability of immobilized enzymes by using nanostructures. It appears to be reasonable to expect that progress in nanostructured biocatalysts will play a critical role in overcoming the major obstacles in the development of powerful biofuel cells.

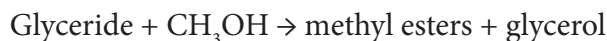
See also: Biochemical Conversion, Bioconversion, Bioplatfrom, Enzymatic Hydrolysis Fermentation.

Esterification

Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow, and waste oils. There are three basic routes to biodiesel production from oils and fats: (i) base-catalyzed transesterification of the oil, (ii) direct acid-catalyzed transesterification of the oil, and (iii) conversion of the oil to its fatty acids and then to biodiesel.

Almost all biodiesel is produced using base-catalyzed transesterification as this is the most economical process. It requires only low temperatures and pressures and produces a 98% conversion yield. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long-chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel, and crude glycerol. In most cases, methanol or ethanol is the alcohol used, where methanol produces methyl esters, and ethanol produces ethyl esters. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production. Either base catalyst can be used for the methyl ester. A common product of the transesterification process is rape methyl ester (RME) produced from raw rapeseed oil reacted with methanol.

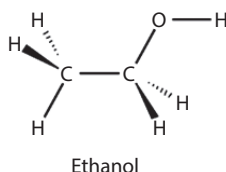
The reaction between the fat or oil and the alcohol is a reversible reaction so that alcohol must be added in excess to drive the reaction toward the right and ensure complete conversion. The products of the reaction are the biodiesel itself and glycerol. Put simply, the equation is:



A successful transesterification reaction is signified by the separation of the ester and glycerol layers after the reaction time. The heavier co-product, glycerol, settles out and may be sold as it is, or it may be purified for use in other industries, e.g., the pharmaceutical, cosmetics industries. Biodiesel is a less toxic and more biodegradable fuel than is crude oil diesel and is often blended with crude oil diesel to provide a renewable energy component in the fuel.

Ethanol

Ethanol (ethyl alcohol, alcohol, grain-spirit; C_2H_5OH) is a clear, colorless, flammable oxygenated hydrocarbon.



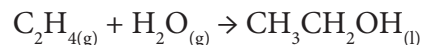
Ethanol (Table E-4) is a volatile, flammable, colorless liquid that has a strong characteristic odor. It burns with a smokeless blue flame that is not always visible in normal light. The physical properties of ethanol stem primarily from the presence of the hydroxyl group and the shortness of its carbon chain. The hydroxyl group is able to participate in hydrogen bonding, rendering it more viscous and less volatile than less polar organic compounds of similar molecular weight.

Table E-4 Selected properties of ethanol compared to methanol.

Property	Ethanol	Methanol
Formula	C_2H_5OH	CH_3OH
Appearance	Colorless liquid	Colorless liquid
Molecular formula	C_2H_6O	CH_4O
Molecular weight	46	32
Specific gravity	0.788 (25°C)	0.789 ((25°C)
Vapor density relative to air	1.59	1.10
Liquid density ($g\ cm^{-3}$ at 25°C)	0.79	0.79
Boiling point (°C)	78	65
Melting point (°C)	-144	-98
Vapor pressure @ 100°C (psia)	2.5	4.6
Heat of evaporation (Btu/lb)	410	472
Heating value (kBTU gallon ⁻¹)		
Lower (LHV)	74	58
Upper (UHV)	85	65
Tank design pressure (psig)	15	15
Viscosity (cp)	1.20	0.54
Flash point (K)	287	284
Flammability/explosion limits		
- (%) Lower (LFL)	3.3	6.7
- (%) Upper (UFL)	19	36
Auto ignition temperature (K)	636	733
Solubility in water (%)	Miscible (100%)	Miscible(100%)
Azeotrope with water	95% v/v EtOH	None

Ethanol is used as a vehicle fuel by itself (E100 is 100% ethanol by volume), blended with gasoline (E85 is 85% ethanol by volume), or as a gasoline octane enhancer and oxygenate (10% by volume).

Ethanol is produced both as a petrochemical, through the hydration of ethylene, and biologically, by fermenting sugars with yeast. Ethanol for use as industrial feedstock is most often made from petrochemical feed stocks, typically by the acid-catalyzed hydration of ethylene:



The catalyst is most commonly phosphoric acid, adsorbed onto a porous support such as diatomaceous earth or charcoal. The reaction is carried out with an excess of high pressure steam at 300°C (570°F).

Ethanol is miscible with water and with many organic solvents, including acetic acid, acetone, benzene, carbon tetrachloride, chloroform, diethyl ether, ethylene glycol, glycerol, nitromethane, pyridine, and toluene. It is also miscible with low-boiling aliphatic hydrocarbon derivatives, such as pentane and hexane, and with aliphatic chlorides such as trichloroethane and tetrachloroethylene. The miscibility of ethanol with water contrasts with that of longer-chain alcohols (five or more carbon atoms), whose water miscibility decreases sharply as the number of carbons increases.

Hydrogen bonding causes pure ethanol to be hygroscopic to the extent that it readily absorbs water from the air. The polar nature of the hydroxyl group causes ethanol to dissolve many ionic compounds, notably sodium and potassium hydroxides, magnesium chloride, calcium chloride, ammonium chloride, ammonium bromide, and sodium bromide. Sodium and potassium chlorides are slightly soluble in ethanol. Because the ethanol molecule also has a nonpolar end, it will also dissolve nonpolar substances, including most essential oils and numerous flavoring, coloring, and medicinal agents.

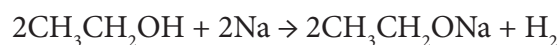
Ethanol-water mixtures have less volume than the sum of their individual components – for example, mixing equal volumes of ethanol and water results in only 1.92 volumes of mixture. The addition of even a few percent of ethanol to water sharply reduces the surface tension of water. This property partially explains the tears of wine phenomenon. When wine is swirled in a glass, ethanol evaporates quickly from the thin film of wine on the wall of the glass. As the ethanol content of the wine decreases, the surface tension increases and the thin film forms beads and runs down the glass in channels rather than as a smooth sheet.

Mixtures of ethanol and water that contain more than approximately 50% ethanol are flammable and easily ignited. An alcohol stove has been developed in India which runs on 50% ethanol/water mixture. Alcoholic proof is a widely used measure of how much ethanol (i.e., alcohol) such a mixture contains. In the 18th century, proof was determined by adding liquor (such as rum) to gunpowder. If the gunpowder still just exploded, that was considered to be 100 degrees proof that it was good liquor; hence, it was called 100 degrees proof.

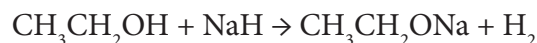
Ethanol-water solutions that contain less than 50% ethanol may also be flammable if the solution is first heated. Some cooking methods call for wine to be added to a hot pan, causing it to flash boil into a vapor, which is then ignited to burn off excess alcohol. Ethanol is slightly more refractive than water, having a refractive index of 1.36242 (at $\lambda = 589.3$ nm and 18.35 °C).

Ethanol is classified as a primary alcohol, meaning that the carbon to which its hydroxyl group is attached has at least two hydrogen atoms attached to it as well and the chemistry of ethanol is largely that of the hydroxyl group.

Ethanol can be quantitatively converted to its conjugate base, the ethoxide ion ($\text{CH}_3\text{CH}_2\text{O}^-$), by reaction with an alkali metal such as sodium:

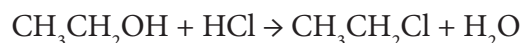


Or a strong base such as sodium hydride:

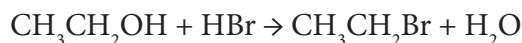


This reaction is not possible in an aqueous solution, as water is more acidic, so that hydroxide is preferred over ethoxide formation.

Ethanol reacts with hydrogen halides to produce ethyl halides such as ethyl chloride and ethyl bromide:

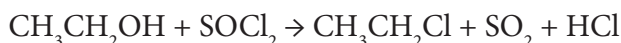


Reaction with hydrogen chloride requires a catalyst such as zinc chloride. Hydrogen chloride in the presence of their respective zinc chloride is known as Lucas reagent.

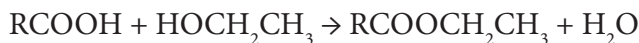


Hydrogen bromide requires refluxing with a sulfuric acid catalyst.

Ethyl halides can also be produced by reacting ethanol with more specialized halogenating agents, such as thionyl chloride for preparing ethyl chloride, or phosphorus tribromide for preparing ethyl bromide.



Under acid-catalyzed conditions, ethanol reacts with carboxylic acids to produce ethyl esters and water:



For this reaction to produce useful yields, it is necessary to remove water from the reaction mixture as it is formed.

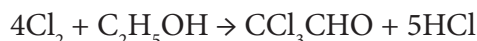
Strong acid desiccants, such as sulfuric acid, cause the dehydration of ethanol to form either diethyl ether or ethylene:



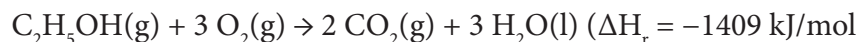
The actual product, diethyl ether or ethylene, predominates depends on the precise reaction conditions.

Ethanol can be oxidized to acetaldehyde, and further oxidized to acetic acid. In the human body, these oxidation reactions are catalyzed by enzymes.

When exposed to chlorine, ethanol is both oxidized and its alpha carbon chlorinated to form the compound, chloral.



Combustion of ethanol forms carbon dioxide and water:



See also: Alcohols, E85.

Ethanol Production

Ethanol is produced from the fermentation of sugar by enzymes produced from specific varieties of yeast. The five major sugars are the five-carbon xylose and arabinose and the six-carbon glucose, galactose, and mannose. Traditional fermentation processes rely on yeasts that convert six-carbon sugars to ethanol. Glucose, the preferred form of sugar for fermentation, is contained in both carbohydrates and cellulose. Because carbohydrates are easier

than cellulose to convert to glucose, the majority of ethanol currently produced in the United States is made from corn, which produces large quantities of carbohydrates. Also, the organisms and enzymes for carbohydrate conversion and glucose fermentation on a commercial scale are readily available.

The conversion of cellulosic biomass to ethanol parallels the corn conversion process. The cellulose must first be converted to sugars by hydrolysis and then fermented to produce ethanol. Cellulosic feedstocks (composed of cellulose and hemicellulose) are more difficult to convert to sugar than are carbohydrates. Two common methods for converting cellulose to sugar are dilute acid hydrolysis and concentrated acid hydrolysis, both of which use sulfuric acid.

Dilute acid hydrolysis occurs in two stages to take advantage of the differences between hemicellulose and cellulose. The first stage is performed at low temperature to maximize the yield from the hemicellulose, and the second, higher temperature stage, is optimized for hydrolysis of the cellulose portion of the feedstock. Concentrated acid hydrolysis uses a dilute acid pretreatment to separate the hemicellulose and cellulose. The biomass is then dried before the addition of the concentrated sulfuric acid. Water is added to dilute the acid and then heated to release the sugars, producing a gel that can be separated from residual solids. Column chromatographic is used to separate the acid from the sugars.

Both the dilute and concentrated acid processes have several drawbacks. Dilute acid hydrolysis of cellulose tends to yield a large amount of by-products. Concentrated acid hydrolysis forms fewer by-products, but for economic reasons, the acid must be recycled. The separation and concentration of the sulfuric acid adds more complexity to the process. The concentrated and dilute sulfuric acid processes are performed at high temperatures (100 and 220°C, 212 to 430°F) which can degrade the sugars, reducing the carbon source and ultimately lowering the ethanol yield. Thus, the concentrated acid process has a smaller potential for cost reductions from process improvements such as acid recovery, and sugar yield for the concentrated acid process could provide higher efficiency for both technologies.

Another approach involves countercurrent hydrolysis, a two-stage process. In the first stage, cellulose feedstock is introduced to a horizontal co-current reactor with a conveyor. Steam is added to raise the temperature to 180°C (no acid is added at this point). After a residence time of approximately 8 minutes, during which some 60% of the hemicellulose is hydrolyzed, the feed exits the reactor. It then enters the second stage through a vertical reactor operated at 225°C (435°F). Very dilute sulfuric acid is added to the feed at this stage, where virtually all of the remaining hemicellulose and, depending on the residence time, anywhere from 60% to all of the cellulose is hydrolyzed. The countercurrent hydrolysis process offers higher efficiency (and, therefore, cost reductions) than the dilute sulfuric acid process. This process may allow an increase in glucose yields to 84%, an increase in fermentation temperature to 55°C (130°F), and an increase in fermentation yield of ethanol to 95%.

The greatest potential for ethanol production from biomass, however, lies in enzymatic hydrolysis of cellulose. The enzyme cellulase, now used in the textile industry to stone wash denim and in detergents, simply replaces the sulfuric acid in the hydrolysis step. The cellulase can be used at lower temperatures, 30 to 50°C, which reduces the degradation of the sugar. In addition, process improvements now allow simultaneous saccharification and fermentation (SSF). In the saccharification and fermentation process, cellulase and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step.

Once the hydrolysis of the cellulose is achieved, the resulting sugars must be fermented to produce ethanol. In addition to glucose, hydrolysis produces other six-carbon sugars from cellulose and five-carbon sugars from hemicellulose that are not readily fermented to ethanol by naturally occurring organisms. They can be converted to ethanol by genetically engineered yeasts that are currently available, but the ethanol yields are not sufficient to make the process economically attractive. It also remains to be seen whether the yeasts can be made hardy enough for production of ethanol on a commercial scale.

See also: Ethanol from Corn, Ethanol Production, Fermentation.

Ethanol Production – Feedstocks

A large variety of feedstocks is currently available for producing ethanol from cellulosic biomass. The materials being considered can be categorized as agricultural waste, forest residue, and energy crops. Agricultural waste available for ethanol conversion includes crop residues such as wheat straw, corn stover (leaves, stalks, and cobs), rice straw,

and bagasse (sugar cane waste). Forestry waste includes underutilized wood and logging residues; rough, rotten, and salvable dead wood; and excess saplings and small trees. Energy crops, developed and grown specifically for fuel, include fast-growing trees, shrubs, and grasses such as hybrid poplars, willows, and switchgrass.

Although the choice of feedstock for ethanol conversion is largely a cost issue, feedstock selection has also focused on environmental issues. Materials normally targeted for disposal include forest thinnings collected as part of an effort to improve forest health, and certain agricultural residues, such as rice straw. Although forest residues are not large in volume, they represent an opportunity to decrease the fire hazard associated with the dead wood present in many forests. Small quantities of forest thinnings can be collected at relatively low cost, but collection costs rise rapidly as quantities increase.

Agricultural residues, in particular corn stover, represent a tremendous resource base for biomass ethanol production. Agricultural residues, in the long term, would be the sources of biomass that could support substantial growth of the ethanol industry. At conversion yields of around 60 to 100 gallons per dry ton, the available corn stover inventory would be sufficient to support 7 to 12 billion gallons of ethanol production per year.

The cost of agricultural residues is not nearly as sensitive to supply as is the cost of forest residues, although the availability of corn stover could be affected by a poor crop year. The relatively low rise in cost as a function of feedstock use is due to the relatively high density of material available that does not involve competition for farmland. In addition, the feedstock is located in the corn-processing belt, an area that has an established infrastructure for collecting and transporting agricultural materials. It is also located near existing grain ethanol plants, which could be expanded to produce ethanol from stover. Initially, locally available labor and residue collection equipment might have to be supplemented with labor and equipment brought in from other locations for residue harvesting and storage operations if the plants involved are of sufficient scale. Eventually, however, when the local collection infrastructure has been built up, costs would come down.

Dedicated energy crops such as switchgrass, hybrid willow, and hybrid poplar are another long-term feedstock option. Switchgrass is grown on a 10-year crop rotation basis, and harvest can begin in year 1 in some locations and year 2 in others. Willows require a 22-year rotation, with the first harvest in year 4 and subsequent harvests every 3 years thereafter. Hybrid poplar requires 6 years to reach harvest age in the Pacific Northwest, 8 years in the Southeast, Southern Plains, and South Central regions, and 10 years in the Corn Belt, Lake States, Northeast, and Northern Plains regions. Thus, if it were planted in the spring of 2000, switchgrass could be harvested in 2000 or 2001, willow could be harvested in 2004, and poplars could be harvested in 2006, 2008, or 2010, depending on the region.

The use of cellulosic biomass in the production of ethanol also has environmental benefits. Converting cellulose to ethanol increases the net energy balance of ethanol compared to converting corn to ethanol. The net energy balance is calculated by subtracting the energy required to produce a gallon of ethanol from the energy contained in a gallon of ethanol (approximately 76,000 Btu). Corn-based ethanol has a net energy balance of 20,000 to 25,000 Btu per gallon, whereas cellulosic ethanol has a net energy balance of more than 60,000 Btu per gallon. In addition, cellulosic ethanol use can reduce greenhouse gas emissions. Cellulosic ethanol can produce an 8 to 10% reduction in greenhouse gas emissions when used in E10 and a 68 to 91% reduction when used in E85.

Ethanol Production – From Corn

The production of ethanol from corn is a mature technology that holds much potential. Substantial cost reductions may be possible, however, if cellulose-based feedstocks are used instead of corn.

Producers are experimenting with units equipped to convert cellulose-based feedstocks, using sulfuric acid to break down cellulose and hemicellulose into fermentable sugar. Although the process is expensive at present, advances in biotechnology could decrease conversion costs substantially. The feed for all ethanol fermentations is sugar - traditionally a hexose sugar (a six-carbon sugar or C6 sugar) such as those present naturally in sugar cane, sugar beet, and molasses. Sugar for fermentation can also be recovered from starch, which is actually a polymer of hexose sugars (polysaccharide).

Biomass, in the form of wood and agricultural residues such as wheat straw, is viewed as a low-cost renewable feed to sugar and starch. It is also potentially available in far greater quantities than sugar and starch feeds. As such, it receives significant attention as a feed material for ethanol production. Like starch, wood and agricultural residues

contain polysaccharides. However, unlike starch, while the cellulose fraction of biomass is principally a polymer of easily fermented C6 sugars, the hemicellulose fraction is principally a polymer of C5 sugars; with quite different characteristics for recovery and fermentation, the cellulose and hemicellulose in biomass are bound together in a complex framework of crystalline organic material known as lignin.

These differences mean that recovery of these biomass sugars is more complex than recovery of sugars from a starch feed. Once recovered, fermentation is also more complex than a simple fermentation of C6 sugars. The current focus focuses on the issues of releasing the sugars (hydrolysis) and then fermenting as much of the C6 and C5 sugars as possible to produce ethanol.

There are several different methods of hydrolysis such as (i) concentrated sulfuric acid, (ii) dilute sulfuric acid, and (iii) nitric acid, and acid pretreatment followed by enzymatic hydrolysis.

See also: Ethanol, Dry Milling, Fermentation, Wet Milling.

Ethanol Production – From Lignocellulosic Feedstocks

The production of ethanol from lignocellulosic biomass such as agricultural and forestry residues, municipal solid waste, and energy crops could improve energy security, reduce trade deficits, decrease urban air pollution, and contribute little, if any, net carbon dioxide accumulation to the atmosphere.

Dilute acid can open up the biomass structure for subsequent processing. The simultaneous saccharification and fermentation (SSF) process is favored for producing ethanol from the major fraction of lignocellulosic biomass, cellulose, because of its low- cost potential. Technology has also been developed for converting the second largest biomass fraction, hemicellulose, into ethanol. The remaining fraction, containing mostly lignin, can be burned as boiler fuel to power the conversion process and generate extra electricity to export.

The production of ethanol from lignocellulosic biomass can be achieved through two different processing routes. They are (i) the biochemical route in which enzymes and other micro-organisms are used to convert cellulose and hemicellulose components of the feedstocks to sugars prior to their fermentation to produce ethanol, and (ii) the thermochemical route in which pyrolysis/gasification technologies produce a synthesis gas ($\text{CO} + \text{H}_2$) from which a wide range of long carbon chain biofuels, such as synthetic diesel or aviation fuel, can be reformed. Lignocellulosic biomass consists mainly of lignin and the polysaccharides cellulose and hemicellulose. Compared with the production of ethanol from first-generation feedstocks, the use of lignocellulosic biomass is more complicated because the polysaccharides are more stable and the pentose sugars are not readily fermentable by *Saccharomyces cerevisiae*. As another example, lignocellulose can be converted to ethanol by the hydrolysis route (Figure E-2):

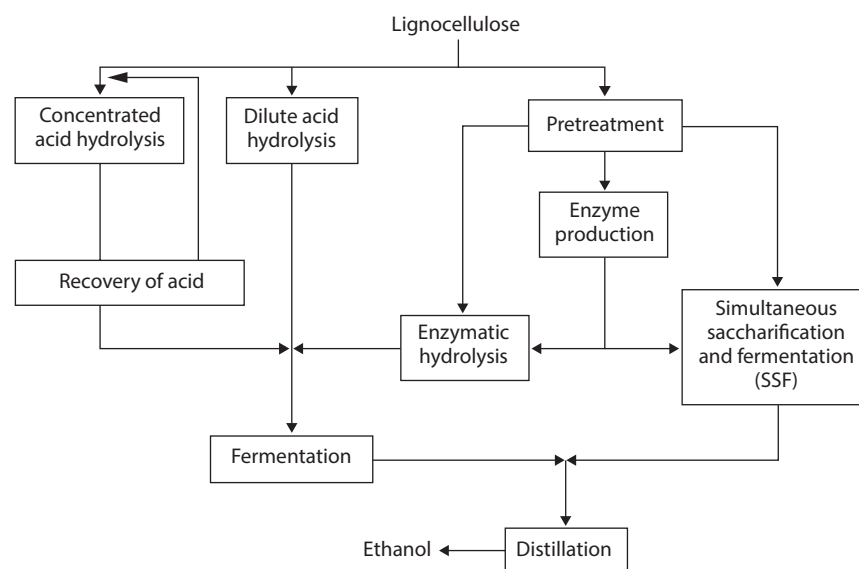


Figure E-2 Ethanol production for lignocellulosic biomass.

However, the conversion efficiency as well as ethanol yield of the biomass differs greatly with respect to the source and nature of the lignocellulosic biomass, primarily due to the variation in lignocellulosic content. Two major polysaccharides in lignocellulosic biomass, namely, cellulose and hemicellulose, firmly link to lignin and form a complex lignocellulosic network, which is highly robust and recalcitrant to depolymerization. For this reason, generation of ethanol from lignocellulosic biomass requires a complicated conversion process that has made it commercially non-competitive. As attempts to exploit lignocellulosic biomass into commercial ethanol production, recent research efforts have been devoted to the techno-economic improvements of the overall conversion process, in addition to screen out promising feedstocks.

Ethanol Production – From Wood

Ethanol produced from various lignocellulosic materials such as wood, agricultural and forest residues has the potential to be a valuable substitute for, or complement to, gasoline.

Ethanol can be produced from lignocellulosic materials in various ways. All processes comprise the same main components: hydrolysis of the hemicellulose and the cellulose to monomer sugars, fermentation and product recovery, and concentration by distillation. The main difference between the process alternatives is the hydrolysis steps, which can be performed by dilute acid, concentrated acid, or enzymatically. Some of the process steps are more or less the same, independent of the hydrolysis method used. For example, enzyme production will be omitted in an acid-hydrolysis process; likewise, the recovery of acid is not necessary in an enzyme-hydrolysis process.

Acid hydrolysis can be performed with several types of acids, including sulfurous, sulphuric, hydrochloric, hydrofluoric, phosphoric, nitric, and formic acid. These acids may be either concentrated or diluted. Processes involving concentrated acids are operated at low temperature and give high yields (e.g., 90% of theoretical glucose yield), but the large amount of acids used causes problems associated with equipment corrosion and energy-demanding acid recovery. Furthermore, when sulphuric acid is used, the neutralization process produces large amounts of gypsum (calcium sulfate, CaSO_4).

The main advantage of dilute acid hydrolysis is the relatively low acid consumption. However, high temperatures are required to achieve acceptable rates of conversion of cellulose to glucose, and high temperatures also increase the rates of hemicellulose sugar decomposition and equipment corrosion. Sugar degradation products can also cause inhibition in the subsequent fermentation stage. The maximum yield of glucose is obtained at high temperature and short residence time, but even under these conditions, the glucose yield is only between 50% and 60% of the theoretical value.

A two-stage process has been developed to decrease sugar degradation. In the first hydrolysis stage, the relatively easily hydrolyzed hemicellulose is released under rather mild conditions. This enables the second acid hydrolysis step to proceed under harsher conditions without degrading the hemicellulose sugars to furfural, hydroxymethyl furfural, and other degradation products.

Ethanol Production - Yields

The variations in organic composition of biomass require thorough consideration to obtain high product yields from a microbial conversion process. In fermentation processes, the lignocellulosic complex is naturally resistant to hydrolysis, so woody and herbaceous biomass often requires significant preparation and pre-treatment. During pre-treatment, weak acids may be used to dissolve and hydrolyze the hemicellulose, leaving a solid residue of cellulose and lignin. Next, the cellulose may be separated and reduced through enzymatic hydrolysis, leaving behind the insoluble lignin. The lignin may then be removed, dried, and burned to provide heat for the process. After the cellulose and hemicellulose are hydrolyzed to simple sugars, microbial conversion uses yeast or bacteria to ferment the sugars, converting them to ethanol, methane, and/or other chemicals.

Cellulose and hemicellulose are composed of different types of sugars that possess different chemical properties. For example, the primary sugar component of cellulose is glucose, a type of hexosan (a polysaccharide yielding only hexose sugar derivatives on hydrolysis). Hemicellulose is primarily xylose, which is a type of pentosan (any

of various polysaccharides that yield only 5-carbon sugar derivatives on hydrolysis). As a result, the cellulose and hemicellulose must be extracted and hydrolyzed through separate processes. Furthermore, different microbes specialize in fermenting specific sugars, so different fermentative organisms are often needed to convert the hexosan derivatives and pentosan derivatives into fuel to achieve a high product yield. Hydrolysis of the holocellulose (the collective term for cellulose and hemicellulose) also produces varying amounts of mannose, galactose, and arabinose sugars, depending on the types of plants in the feedstock.

Sugars require specific enzymes to convert each of them into ethanol and other products. To maximize product yield from a microbial conversion process, it is important to analyze the sugar composition of the feedstock and tailor the enzymes used in the conversion process to optimize fermentation of the specific sugar constituents according to their relative proportions.

Certain microbes can rapidly generate high product yields from xylose and glucose, the primary sugar constituents in commonly available biomass feedstocks. Most fermentative organisms specialize in digesting particular sugars, and few produce the enzymes needed to directly ferment xylose or arabinose. Recently, several strains of yeast and bacteria have been genetically engineered to digest the sugar components of both cellulose and hemicellulose.

Yeast tends to be a very robust organism in ethanol conversion processes, but bacteria, which have the potential to be more efficient, are more susceptible to weak acids and other feed stream toxins such as chemical extractives. Softwoods evolved higher levels of gums and resins that inhibit fungal or bacterial growth. As a result, softwoods and hardwoods usually require distinct enzymatic or microbial conversion processes for optimal yields.

In the conversion of cellulose to ethanol, the approximate ethanol yield per ton of feedstock is a function of three variables: the weight fraction of holocellulose in the feedstock, the fraction of cellulose in the total carbohydrates, and the fraction of total carbohydrates converted to ethanol.

For example, if the feedstock contains 70% holocellulose, of which 80% is converted to ethanol, then the estimated yield is approximately 95 gallons per ton. The fraction of cellulose in the total carbohydrates tends to have a minor effect on ethanol yield in this process. Lignin is insoluble and is left behind as a solid residue after chemical and microbial conversion. The lignin is not easily reduced or fermented and is sometimes wasted, but it has similar heat content to low-grade coal (approximately 10,000-12,000 Btu/lb) and may be dried and burned as fuel in cogeneration systems.

Assuming that most of the remaining 30% of the feedstock in the above example is lignin, enough material can be burned to provide the heat and electricity to power the entire conversion process, as well as excess electricity that can be sold for additional revenue.

Ethyl Alcohol

See also: Ethanol.

Evaporation

Evaporation is the process by which molecules in a liquid state spontaneously become gaseous and is the opposite of condensation. Generally, evaporation can be seen by the gradual disappearance of a liquid when exposed to a significant volume of gas. Typically, the molecules do not have enough energy to escape from the liquid, or else the liquid would turn into vapor quickly. When the molecules collide, they transfer energy to each other in varying degrees, based on how they collide. Sometimes, the transfer is so one-sided for a molecule near the surface that it ends up with enough energy to escape.

Evaporation is the opposite of condensation and sublimation and is the phenomenon that occurs when a liquid is transformed to gas without chemical alteration and the conversion of the solid to a liquid and thence the liquid to a gas. Evaporation (the conversion of a liquid to a gas) which is one of several phase transformations that can occur after a chemical is released into the environment (Table E-5) should not be confused with sublimation in which a solid is transferred directly to a gas:

Evaporation:

Liquid → gas

Sublimation:

Solid → gas

Table E-5 Examples of phase transformations.

From	To	Process
Gas	Gas	N/A*
Gas	Liquid	Condensation
Gas	Solid	Deposition
Liquid	Gas	Evaporation or boiling
Liquid	Liquid	N/A*
Liquid	Solid	Freezing
Solid	Gas	Sublimation
Solid	Liquid	Melting
Solid	Solid	Transformation**

*May involve a chemical change depending upon the temperature and pressure

** For example, a change in crystal structure

Both phenomena are important parts of the environmental chemical cycle since both processes involve the disappearance of a contaminant in the water or on the land *but* the contaminant does appear in the atmosphere. Of the two processes, the evaporation is the most common process since chemicals that go through the sublimation processes are not as obvious or as common as chemicals that evaporate. In the field of environmental chemistry, evaporation is more typical when water evaporated from an aqueous solution of the chemical rather than evaporation (volatilization) of the chemical.

Liquids that do not evaporate visibly at a given temperature in a given gas (e.g., cooking oil at room temperature) have molecules that do not tend to transfer energy to each other in a pattern sufficient to frequently give a molecule the heat energy necessary to turn into vapor.

If evaporation takes place in a closed vessel, the escaping molecules accumulate as a vapor above the liquid. Many of the molecules return to the liquid, with returning molecules becoming more frequent as the density and pressure of the vapor increases. When the process of escape and return reaches an equilibrium, the vapor is *saturated*, and no further change in either vapor pressure and density or liquid temperature will occur. For a system consisting of vapor and liquid of a pure substance, the equilibrium state is related to the vapor pressure of the substance (Clausius-Clapeyron equation):

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

P_1 and P_2 are the vapor pressures at temperatures T_1 and T_2 , respectively, ΔH_{vap} is the enthalpy of vaporization, and R is the universal gas constant.

The ability for a molecule of a liquid to evaporate is largely based on the amount of kinetic energy an individual particle may possess. Even at lower temperatures, individual molecules of a liquid can evaporate if they have more than the minimum amount of kinetic energy required for vaporization. The factors which influence the rate of evaporation are: (i) the concentration of the substance evaporating in the air – if the air already has a high concentration of the substance evaporating, then the given substance will evaporate more slowly, (ii) the concentration of other

substances in the air – if the air is already saturated with other substances, it can have a lower capacity for the substance evaporating, (iii) the concentration of other substances in the liquid (impurities) – if the liquid contains other substances, it will have a lower capacity for evaporation, (iv) the flow rate of air – if fresh air is moving over the substance all the time, then the concentration of the substance in the air is less likely to increase with time, thus encouraging faster evaporation, (v) the inter-molecular forces – the stronger the forces keeping the molecules together in the liquid state, the more energy one must get to escape, (vi) the pressure – in an area of less pressure, evaporation happens faster because there is less exertion on the surface keeping the molecules from launching themselves, (vii) the surface area – a substance which has a larger surface area will evaporate faster as there are more surface molecules which are able to escape, (viii) the temperature – if the liquid is hotter, evaporation is more rapid, and (ix) the density – the higher the density, the slower a liquid evaporates.

However, many factors affect the evaporation process. For example, if the air is already saturated with other chemicals (or the humidity is high when the water content is high), there is typically little chance of a liquid evaporating as quickly as when the air is not saturated (or humidity is low). In addition, the air pressure also affects the evaporation process since, under high air pressure, a chemical is much more difficult to evaporate. Temperature also affects the ability of a chemical to evaporate.

See also: Distillation, Evaporation Processes.

Evaporation Processes

Evaporation processes are the final steps for concentrating solid residues. It is generally accomplished in evaporation basins, which are simply lined ponds into which the sludge is pumped and allowed to stand while the moisture evaporates, or in sludge drying beds, which contain a layer of coarse sand over a layer of fine sand over clay or perforated plastic drainage tiles. Both systems require large areas of land compared to other more compact devices such as vacuum filtration, but they are inexpensive and require little maintenance. Sludge drying beds are faster but more expensive. Both systems require mechanical removal of the dried sludge, usually with a backhoe or front-loader.

Falling film vertical tube evaporators have the highest heat transfer characteristics of all evaporator types. A high heat transfer coefficient is needed to efficiently evaporate the water and save energy. The vertical tube, falling film arrangement, also allows evaporation to occur with reduced fouling effects by keeping surfaces wetted at all times. Distributors are used to ensure an even falling film in these evaporators. Zero liquid discharge, if required, is attainable with the evaporative produced water treatment approach.

See also: Distillation, Evaporation.

Exosphere

The exosphere is the outermost layer of the atmosphere (that is, it is the upper limit of the atmosphere) and extends from the exobase, which is located at the top of the thermosphere. The exosphere begins variously from approximately 2,300,000 ft to 3,280,000 ft above the surface, where it interacts with the magnetosphere, to space. Each of the layers has a different lapse rate, defining the rate of change in temperature with height. Initial atmospheric composition is generally related to the chemistry and temperature of the local solar nebula during planetary formation and the subsequent escape of interior gases. The exosphere is an atmosphere so thin that its few atoms or molecules are unlikely to collide with one another. In the atmosphere of the Earth, the exosphere is the highest part of the atmosphere where the density of gas molecules is low.

The exosphere layer is mainly composed of extremely low densities of hydrogen, helium, and several heavier molecules including nitrogen, oxygen, and carbon dioxide closer to the exobase. The atoms and molecules are so far apart that they can travel hundreds of kilometers without colliding with one another. Thus, the exosphere no longer behaves like a gas, and the particles constantly escape into space. The exosphere contains most of the satellites orbiting Earth.

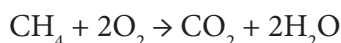
The highly attenuated gas in this layer can reach a temperature on the order of 2,500°C (4,530°F) during the day. Despite the high temperature, an observer or object will experience cold temperatures in the thermosphere, because

the extremely low density of gas (practically a high vacuum) is insufficient for the molecules to conduct heat. In the anacoustic zone (above 99 miles), the density is so low that molecular interactions are too infrequent to permit the transmission of sound.

See also: Atmosphere.

Exothermic Reaction

An exothermic reaction is a chemical reaction process in which heat is evolved. Combustion or burning of a fuel is a complex sequence of exothermic chemical reactions between a fuel (usually a hydrocarbon) and an oxidant accompanied by the production of heat or both heat and light.



The energy needed for the reaction to occur is less than the total energy released (Figure E-3).

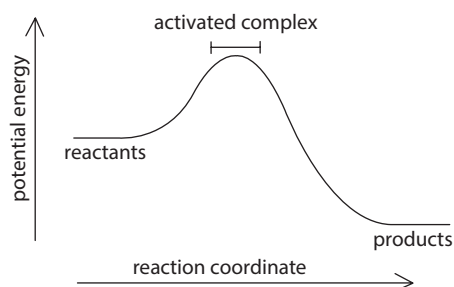
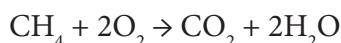


Figure E-3 Representation of an exothermic reaction in which the heat content of the products is greater than the heat content of the reactants.

For an exothermic reaction, this gives a negative value for ΔH , since a larger value (the energy released in the reaction) is subtracted from a smaller value (the energy used for the reaction).

In a chemical reaction, reactants are converted into products by the breaking and making of chemical bonds. Bond breaking requires energy, while bond making releases energy. The balance between the two gives a positive or negative energy change for the reaction, and chemical reactions are classed as being either endothermic, with a positive energy change, or exothermic, with a negative energy change. Thus, an exothermic reaction is a chemical reaction that produces heat.

Combustion or burning of a fuel is a complex sequence of exothermic chemical reactions between a fuel (usually a hydrocarbon) and an oxidant accompanied by the production of heat or both heat and light.



See also: Endothermic Reaction.

Explosive Limits

The explosive limit of a gas or a vapor is the limiting concentration (in air) that is needed for the gas to ignite and explode. There are two explosive limits for any gas or vapor, the lower explosive limit (LEL) and the upper explosive limit (UEL). A fuel and oxygen (air) must exist in certain proportions, along with an ignition source, such as a spark or flame. The ratio of fuel and oxygen that is required varies with each combustible gas or vapor. The minimum concentration of a particular combustible gas or vapor necessary to support its combustion in air is the *lower explosive limit* (LEL) for that gas. Below this level, the mixture is too lean to burn. The maximum concentration of a gas or

vapor that will burn in air is the *upper explosive limit* (UEL). Above this level, the mixture is too rich to burn. The range between the LEL and the UEL is the flammable range for that gas or vapor.

Dusts also have upper and lower explosion limits, though the upper limits are hard to measure and of little practical importance. The LELs for many organic materials are in the range of 10 to 50 g/m³, which is much higher than the limits set for health reasons, as is the case for the LEL of many gases and vapors. Dust clouds of this concentration are hard to see through for more than a short distance, and normally only exist inside process equipment.

See also: Lower Explosive Limit, Lower Flammability Limit, Upper Explosive Limit, Upper Flammability Limit.

Extraction

Extraction is a process in which one or more components are separated selectively from a liquid or solid mixture, the feed (Phase 1), by means of a liquid immiscible solvent (Phase 2). The transfer of the components from the feed to the solvent is controlled by the solubility behavior of each component in the corresponding phase. Two phases result from the extraction step: one enriched (the extract phase) and the other depleted (the raffinate phase) in the components to be separated, respectively. In order to regenerate the solvent, another separation step (e.g., distillation) is finally required.

Liquid-liquid extraction is most widely used and will be considered within this laboratory. It is applied, e.g., to remove heavy metals or acids from wastewater or for the production of aromatic compounds from mixtures of hydrocarbons. Another application is gas-liquid extraction which is also called absorption.

Compared to distillation, extraction processes have the disadvantage that a new component is added to the system. This leads to additional impurities as complete immiscibility does only exist in theory. Furthermore, a subsequent separation process is required to regenerate the solvent. However, there are a number of situations in which extraction is advantageous, and they are: (i) one or more components in the mixture are not thermally stable, (ii) the components in the mixture have a high or low boiling point requiring vacuum or cryogenic distillation, which is very energy intensive, (iii) the boiling points of the components are very close or they form azeotropes, (iv) two components with very different boiling points have to be separated at the same time, and (v) the components to be separated (pollutants or valuable products) are only a small fraction of the mixture.

See also: Absorption, Biomass – Extraction, Distillation, Extractive Distillation.

Extractive Distillation

Extractive distillation is distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, which forms no azeotrope with the other components in the mixture. The method is used for mixtures having a low value of relative volatility, nearing unity. Such mixtures cannot be separated by simple distillation because the volatility of the two components in the mixture is nearly the same, causing them to evaporate at nearly the same temperature at a similar rate, making normal distillation impractical.

In extractive distillation, the solvent is specially chosen to interact differently with the components of the original mixture, thereby altering their relative volatility. Because these interactions occur predominantly in the liquid phase, the solvent is continuously added near the top of the extractive distillation column so that an appreciable amount is present in the liquid phase on all of the trays below. The mixture to be separated is added through second feed point further down the column. In the extractive column, the component having the greater volatility, not necessarily the component having the lowest boiling point, is taken overhead as a relatively pure distillate. The other component leaves with the solvent via the column bottoms. The solvent is separated from the remaining components in a second distillation column and then recycled back to the first column.

It is important to select a suitable separation solvent for this type of distillation. The solvent must alter the relative volatility by a wide enough margin for a successful result. The quantity, cost, and availability of the solvent should be considered. The solvent should be easily separable from the bottom product, and should not react chemically with the components or the mixture, or cause corrosion in the equipment. A classic example to be cited here is the separation of an azeotropic mixture of benzene and cyclohexane, where aniline is one suitable solvent.

Extractive distillation is used to recover aromatic hydrocarbon derivatives from, say, reformat fractions in the following manner. By means of preliminary distillation in a 65-tray pre-fractionator, a fraction containing a single aromatic can be separated from reformat, and this aromatic concentrate is then pumped to an extraction distillation tower near the top and aromatic concentrate enters near the bottom. A reboiler in the extractive distillation tower induces the aromatic concentrate to ascend the tower, where it contacts the descending solvent.

The solvent removes the aromatic constituents and accumulates at the bosom of the tower; the non-aromatic portion of the concentrate leaves the top of the tower and may contain approximately 1% of the aromatics. The solvent and dissolved aromatics are conveyed from the bottom of the extractive distillation tower to a solvent stripper, where fractional distillation separates the aromatics from the solvent as an overhead product. The solvent is recirculated to the extractive distillation tower, whereas the aromatic stream is treated with sulfuric acid and clay to yield a finished product of high purity.

See also: Distillation.

Explosive Limits

The explosive limit of a gas or a vapor is the limiting concentration (in air) that is needed for the gas to ignite and explode. Before a fire or explosion can occur, three conditions must be met simultaneously. A fuel (i.e., combustible gas) and oxygen (air) must exist in certain proportions, along with an ignition source, such as a spark or flame. The ratio of fuel and oxygen that is required varies with each combustible gas or vapor. The minimum concentration of a particular combustible gas or vapor necessary to support its combustion in air is defined as the lower explosive limit (LEL) for that gas. Below this level, the mixture is too lean (dilute) to burn. The maximum concentration of a gas or vapor that will burn in air is defined as the upper explosive limit (UEL). Above this level, the mixture is too rich to burn. The range between the lower explosive limit and the upper explosive limit is known as the flammable range for that gas or vapor. Concentrations of explosive gases are often given in terms of percent of lower explosive limit (%LEL).

Dusts also have upper and lower explosion limits, though the upper limits are hard to measure and of little practical importance. Lower explosive limits for many organic materials are in the range of 10 to 50 g/m³, which is much higher than the limits set for health reasons, as is the case for the lower explosive limit of many gases and vapors. Dust clouds of this concentration are hard to see through for more than a short distance, and normally only exist inside process equipment.

Extra Heavy Crude Oil

Extra heavy crude oil is a non-descript term (related to viscosity) of little scientific meaning that is usually applied to tar sand bitumen, which is generally capable of free flow under reservoir conditions. Thus, the general difference is that extra heavy crude oil, which may have properties similar to tar sand bitumen in the laboratory but, unlike tar sand bitumen in the deposit, has some degree of mobility in the reservoir or deposit.

Extra heavy crude oils can flow at reservoir temperature and can be produced economically, without additional viscosity-reduction techniques, through variants of conventional processes such as long horizontal wells, or multi-laterals. This is the case, for instance, in the Orinoco basin (Venezuela) or in offshore reservoirs of the coast of Brazil, but, once outside of the influence of the high reservoir temperature, these oils are too viscous at surface to be transported through conventional pipelines and require heated pipelines for transportation. Alternatively, the oil must be partially upgraded or fully upgraded or diluted with a low-boiling hydrocarbon fraction (such as aromatic naphtha) to create a mix that is suitable for transportation.

The largest accumulation of extra heavy crude oil is the Venezuelan Orinoco heavy-oil belt, which contains approximately 90% v/v of the world heavy crude oil reserves, when measured on an oil-in-place basis. In addition to extra-heavy Orinoco oil, South America also has technically recoverable heavy crude oil, so that, in total, approximately 61% v/v of the known technically recoverable heavy crude oil is in South America. However, the actual production data for heavy crude oil recovery is difficult to assess because of the loose and often arbitrary definitions that are employed.

See also: Tar Sand.

Extraneous Mineral Matter

Extraneous mineral matter is the mineral matter that was brought into the coal-forming deposit by mechanical means from outside as, for example, dust by air or as mineral matter that was suspended or dissolved and carried by water.

The presence of the mineral matter in coal is even more apparent when the coal is examined in place in the bed, after being mined or finally prepared for market, and, finally, when the residue from its combustion is examined.

Extraneous mineral matter is apparent as definite horizontal layers of varying thickness and extent, as surface deposits or fillings in the vertical cleats, and more unusually as intrusions of clay-like (or other) material which occurs irregularly throughout the coal deposit. The horizontal layers that attain a considerable thickness may serve as a means of separating different coals or simply as separating the different phases of formation of one particular coal. Bands of this type are always regarded as being formed during the deposition of the coal precursors.

The mineral deposits in the shrinkage cracks or cleats, which may, for example, be kaolinite, calcite, gypsum, or pyrite, are usually thick surface deposits and may not always be present and were presumably deposited later in the coal-forming process. The larger adventitious bodies of foreign matter in the coal (such as clay veins, sandstone intrusions, and washouts) may be the result of rather unusual geological conditions during and after the time the coal beds were laid down. A large part of the mineral matter in marketed coal arises from the inclusion during mining of roof (or floor) rock of the impure streaks or of some of the large impurities. Such inclusions may be deliberate insofar as little effort is made to remove them during the mining operation, or they may be accidental in that their elimination during mining was not complete. The increasing use of mechanical methods of mining (particularly in large-scale strip operation) has supported the practice to do little exclusion during mining and to subject the coal to a cleaning process afterward.

ExxonMobil AGC-21 Process

Conversion of natural gas to liquids (GTL) utilizing Fischer-Tropsch (FT) hydrocarbon synthesis technology is an attractive option to bring additional liquids to market. The ExxonMobil advanced gas conversion process for the 21st Century (AGC-21)¹ is state-of-the-art gas-to-liquids technology that provides an option for utilization of gaseous products from biomass.

In the process, there are three key steps. In the first step, syngas is generated by contacting methane with steam and a limited amount of oxygen in a high capacity catalytic reactor. Hydrocarbon derivatives are synthesized in the second step at high alpha in a novel slurry reactor using new, high productivity catalysts operating at high levels of syngas conversion. The full-range, primarily normal paraffin product contains significant 650°F+ waxy material that is a solid at room temperature and melts above 122°C (250°F), unsuitable for pipelining or transporting in conventional crude carriers. The final step, accomplished with proprietary catalysts in a packed bed reactor, converts wax to high-quality liquids that make excellent feeds for refineries and chemical plants and directly marketable products in some instances, such as lube base stocks or specialty solvents.

The chemistry of each step is straightforward yet becomes more complex as processes go to high yield and selectivity. Oxygen, methane, and steam ratios are carefully controlled to produce syngas (carbon monoxide and hydrogen) at stoichiometric proportions of approximately 2.1 to 1 hydrogen to carbon monoxide.

See also: Gasification, Gasifiers, Synthesis Gas.

Fabric Filter

A fabric filter is made from fabric materials and used for removing particulate matter from gas streams. Commonly known as baghouses, fabric collectors use filtration to separate dust particulates from dust-laden gas streams. They are one of the most efficient and cost-effective types of dust collectors available and can achieve a collection efficiency of more than 99% for fine particulate matter.

The filter unit consists of one or more isolated compartments containing rows of fabric bags in the form of round, flat, or shaped tubes, or pleated cartridges. Particle-laden gas passes up (usually) along the surface of the bags then radially through the fabric. Particles are retained on the upstream face of the bags, and the cleaned gas stream is vented to the atmosphere. The filter is operated cyclically, alternating between relatively long periods of filtering and short periods of cleaning. During cleaning, dust that has accumulated on the bags is removed from the fabric surface and deposited in a hopper for subsequent disposal.

As the dusty emissions flow through the filter media (typically cotton, polypropylene, Teflon, or fiberglass), particulate matter is collected on the bag surface as a dust cake. Fabric filters are generally classified based on the filter bag cleaning mechanism employed and operate with collection efficiencies above 99%. The layer of dust, or dust cake, collected on the fabric is primarily responsible for such high efficiency. The cake is a barrier with tortuous pores that trap particles as they travel through the cake. Gas temperatures up to approximately 260°C (500°F), with surges to approximately 285°C (550°F) can be accommodated routinely in some configurations. Most of the energy used to operate the system appears as pressure drop across the bags and associated hardware and ducting.

Fabric filters are used where high-efficiency particle collection is required. Limitations are imposed by gas characteristics (temperature and corrosivity) and particle characteristics (primarily stickiness) that affect the fabric or its operation and that cannot be economically accommodated.

Process variables include particle characteristics, gas characteristics, and fabric properties. The most important design parameter is the air- or gas-to-cloth ratio (the amount of gas in ft³/min that penetrates one ft² of fabric), and the usual operating parameter of interest is pressure drop across the filter system. The major operating feature of fabric filters that distinguishes them from other gas filters is the ability to renew the filtering surface periodically by cleaning.

Fabric filters can be categorized by several means, including type of cleaning (shaker, reverse air, pulse-jet), direction of gas flow (from inside the bag towards the outside or vice versa), location of the system fan (suction or pressure), or size (low, medium, or high gas flow quantity). Of these four approaches, the cleaning method is probably the most distinguishing feature.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Fast-Neutron Reactor

A fast-neutron reactor (FNR, or fast reactor) is a type of nuclear reactor in which the fission chain reactor is sustained by Fast-Neutrons as opposed to thermal neutrons that are the active principle of thermal-neutron reactors. The Fast-Neutron reactor does not need a neutron moderator but does require nuclear fuel that is relatively rich in fissile (fissionable) material when compared to the fuel required for a thermal-neutron reactor.

See also: Nuclear Reactor – Fast-Neutron Reactor.

Fast Pyrolysis

Fast pyrolysis (rapid pyrolysis) is a thermal process in which biomass is rapidly heated to a carefully controlled temperature (approximately 400 to 600°C, 750 to 1,110°F), then very quickly cool the volatile products formed in the reactor. The process offers the unique advantage of producing a liquid that can be stored and transported and has been developed in many configurations. The fast heating rates used in fast pyrolysis allow the conversion of thermally unstable compounds before they produce undesired coke.

Fast pyrolysis units are designed to produce bio-oil by heating biomass to the designated temperature less than one second in the absence of oxygen. The process is not feedstock-specific. Most types of biomass feedstock can be used in the fast pyrolysis process to make bio-oil. There is no change in the process, and the yield and properties of the product are determined by the properties of the feedstock.

One option for the process is to build the pyrolysis unit near to the source and move the bio-oil to a biorefinery. Another benefit is that you can use this technology which is flexible insofar as it does not need chemicals or enzymes that have to be specific to a certain type of biomass feedstock.

Fast pyrolysis is one of the most promising methods for biofuel production. The reaction conditions allow the conversion of thermally unstable biomass compounds to a liquid product (bio-oil) while minimizing undesired reactions (i.e., coke and gas formation). The bio-oils are acidic combustible liquids containing more than 300 compounds that degrade with time.

Addition of heterogeneous catalysis to fast pyrolysis (catalytic fast pyrolysis) has the potential to significantly change the products produced and the product distribution.

See also: Pyrolysis.

Fat Oil

Fat oil is the bottom oil or enriched oil drawn from the absorber (as opposed to lean oil) in a gas cleaning process.

See also: Absorption, Gas Cleaning, Gas Processing, Gas Treating.

Fats And Greases

The proper categorization of fats and greases may be debatable since those are by-products of the reduction of animal biomass into component parts. However, most fats and greases, and some oils, are not available for bioenergy use until after they become a post-consumer waste stream; it seems appropriate for them to be included in the tertiary biomass category. Vegetable oils derived from processing of plant components and used directly for bioenergy (e.g., soybean oil used in biodiesel) would be a secondary biomass resource, though amounts being used for bioenergy are most likely to be tracked together with fats, greases, and waste oils.

The categorization of fats and greases within biomass may be debatable since those are by-products of the reduction of animal biomass into component parts. However, animal fats are a type of biomass, and since most fats and greases, and some oils, are not available for bioenergy use until after they become a post-consumer waste stream, it is appropriate for fats and greases to be included in the tertiary biomass category.

Vegetable oils derived from processing of plant components and used directly for bioenergy (e.g., soybean oil used in biodiesel) would be a secondary biomass resource, though amounts being used for bioenergy are most likely to be tracked together with fats, greases, and waste oils.

See also: Biomass.

Fatty Acids

Until the refining of crude oil was developed during the 19th century, vegetable oils, especially the non-edible varieties (Table F-1), formed an important source of heat and light.

Table F-1 Examples of saturated and unsaturated fatty acids.

Acid*	Carbon atoms	Double bonds
Arachidic	20	0
Behemic	22	0
Caprylic acid	8	0
Capric acid	10	0
Cerotic	26	0
Eicosenoic	20	1
Elaidic	18	1
Erucic	22	1
Lauric	12	0
Lignoceric	24	0
Linoleic	18	2
Myristic	14	0
Oleic	18	1
Palmitic	16	0
Sapienic	16	1
Stearic	18	0

*Listed alphabetically.

Usually, the seeds, which store much higher concentration of fatty oil than any other part of the plant, are used for extracting the oil. Most of the common oil seeds contain 20-30% w/w of the oil and in some cases in excess of 50% w/w (Table F-2).

Table F-2 Percentage of fatty acid types for different oils.

Oil	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3*
Corn	6.0	-	2.0	44.0	48.0	-
Cottonseed	28.3	-	0.9	13.3	57.5	-
Olive	14.6	-	-	75.4	10.0	-
Palm	42.6	0.3	4.4	40.5	10.1	0.2
Peanut	11.4	-	2.4	48.3	32.0	0.9
Rapeseed	3.5	0.1	0.9	54.1	22.3	-
Safflower	7.3	0.1	1.9	13.5	77.0	-
Soybean	11.9	0.3	4.1	23.2	54.2	6.3
Sunflower	6.4	0.1	2.9	17.7	72.9	-
Tallow	29.0	-	24.5	44.5	-	-
WCO**	20.4	4.6	4.8	52.9	13.5	0.8

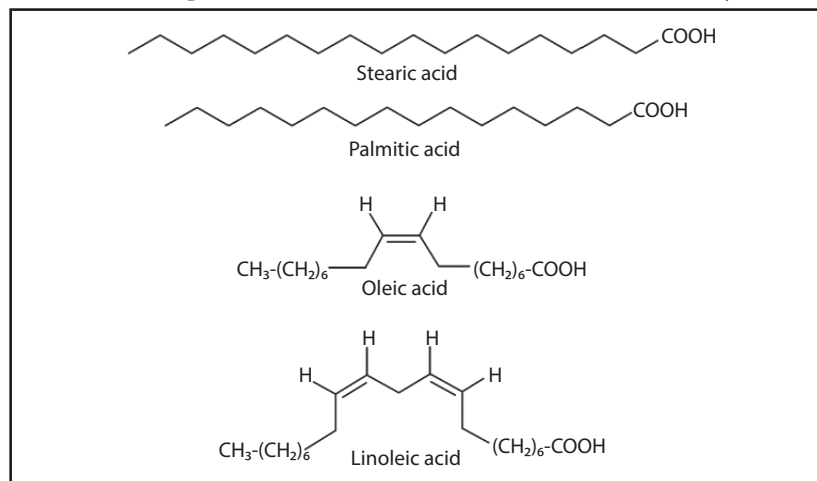
*The first number is the total number of carbon atoms in the acid molecule, and the second number is the carbon atom on which the double bond is located.

**WCO: waste cooking oil.

The techniques for the extraction of oil from the seeds are relatively simple and may involve one or more of the following processes, viz., (i) pressing, (ii) cooking in water, and (iii) solvent extraction. Some of the non-edible oils that are being tried as transport fuel for vehicles are the oils of Pongamia, mahua, neem, and Jatropha.

By way of definition, in chemistry, particularly in biochemistry, a **fatty acid** is a carboxylic acid with a long carbon (aliphatic) chain, which is either saturated or unsaturated. Most naturally occurring fatty acids have an unbranched carbon chain of an even number of carbon atoms, from 4 to 28 carbon atoms (Table F-3).

Table F-3 Examples of the structural characteristics of selected fatty acids.



Unsaturated fatty acids have one or more carbon-carbon ($\text{C}=\text{C}$) double bonds which can confer either *cis* or *trans* isomers.

A *cis* configuration means that the two hydrogen atoms adjacent to the double bond stick out on the same side of the chain. The rigidity of the double bond freezes its conformation and, in the case of the *cis* isomer, causes the chain to bend and restricts the conformational freedom of the fatty acid. The more double bonds the chain has in the *cis* configuration, the less flexibility it has. When a chain has many *cis* bonds, it becomes quite curved in its most accessible conformations. For example, oleic acid, with one double bond, has a slight bend in the molecule whereas linoleic acid, with two double bonds, has a more pronounced bend and alpha-linoleic acid, with three double bonds, favors a hooked shape to the molecule. The effect of this is that, in restricted environments, such as when fatty acids are part of a phospholipid in a lipid bilayer, or triglycerides in lipid droplets, *cis* bonds limit the ability of fatty acids to be tightly packed, and therefore can affect the melting temperature of the membrane or of the fat. *Cis* unsaturated fatty acids, however, increase cellular membrane fluidity, whereas *trans* unsaturated fatty acids do not.

By contrast, a *trans* configuration, by contrast, means that the adjacent two hydrogen atoms lie on *opposite* sides of the chain. As a result, they do not cause the chain to bend much, and their shape is similar to straight saturated fatty acids. In most naturally occurring unsaturated fatty acids, each double bond has three (*n*-3), six (*n*-6), or nine (*n*-9) carbon atoms after it, and all double bonds have a *cis* configuration. Most fatty acids in the *trans* configuration (*trans* fats) are not found in nature and are the result of human processing (such as hydrogenation). The geometric differences between the various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids, play an important role in biological processes, and in the construction of biological structures (such as cell membranes).

Vegetable oils are the esters of glycerol and fatty acids. In this form, they are not quite suitable as substitutes for petrol or diesel, though a mixture of certain percentage (up to 30%) of oil with diesel is found to work reasonably well. However, they can be modified to get more suitable fuels that can fully substitute diesel or petrol. One way is by cracking them at higher temperatures on certain metal oxide catalysts, which yields hydrocarbon derivatives having fuel qualities similar to those of petrol/diesel. The other method is a chemical reaction called transesterification. In this process, the glyceryl esters of the fatty acids in the oil are converted into their methyl esters by an acid-catalyzed reaction of oils with methanol. The methyl esters are better suited to be used as vehicle fuel, either in pure form or by blending with diesel.

See also: Biodiesel, Vegetable Oils.

Feedstock

The feedstock is the raw material for a process that is used to create new products as defined by the process equipment and parameter. The term raw material can encompass the entirety of what goes into making a product. The feedstock is typically a single, uniform, raw material that is given as an input into a process, usually in large quantities. In some cases, the feedstock to a process may be a product for a secondary that has previously been reduced from the original raw feedstock.

Many process units operate continuously (as opposed to batch operation) at steady state or approximately steady state for long periods of time (months to years). The high capacity also makes process optimization and advanced process control desirable.

See also: Refining.

Fermentation

A number of processes allow biomass to be transformed into gaseous fuels such as methane or hydrogen. One pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. A second pathway uses plant material such as agricultural residues in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment, but often with the energy produced only for onsite use, which often implies less than maximum energy yields. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. In addition to biogas, there is also the possibility of using the solid by-product as a biofuel.

Fermentation feedstocks require pretreatment by chemical, physical, or biological means to open up the structure of biomass and reduce the complex carbohydrates to simple sugars. This type of pretreatment is often referred to as hydrolysis. The resulting sugars can then be fermented by the yeast and bacteria employed in the process. Feedstocks high in starch and sugar are most easily hydrolyzed. Cellulosic feedstocks, including the major fraction of organics in MSW, are more difficult to hydrolyze, requiring more extensive pretreatment. Fermentation is generally used industrially to convert substrates such as glucose to ethanol for use in beverage, fuel, and chemical applications and to other chemicals (e.g., lactic acid used in producing renewable plastics) and products (e.g., enzymes for detergents). Strictly speaking, fermentation is an enzymatically controlled anaerobic process although the term is sometimes more loosely applied to include aerobic processing as well.

Traditional fermentation plants producing biogas are in routine use, ranging from farms to large municipal plants. As feedstock, they use manure, agricultural residues, urban sewage, and waste from households, and the output gas is typically 64% methane. The biomass conversion process is accomplished by a large number of different agents, from the microbes decomposing and hydrolyzing plant material, over the acidophilic bacteria dissolving the biomass in aquatic solution, and to the strictly anaerobic methane bacteria responsible for the gas formation. Operating a biogas plant for a period of some months usually makes the bacterial composition stabilize in a way suitable for obtaining high conversion efficiency (typically above 60%, the theoretical limit being near 100%), and it is found important not to vary the feedstock compositions abruptly if optimal operation is to be maintained. Operating temperatures for the bacterial processes are only slightly above ambient temperatures, e.g., in the mesophilic region around 30°C.

The production of ethanol from corn is a mature technology that holds much potential. Substantial cost reductions may be possible, however, if cellulose-based feedstocks are used instead of corn. The feed for all ethanol fermentations is sugar – traditionally a hexose (a six-carbon or “C6” sugar) such as those present naturally in sugar cane, sugar beet, and molasses. Sugar for fermentation can also be recovered from starch, which is actually a polymer of hexose sugars (*polysaccharide*).

Biomass, in the form of wood and agricultural residues such as wheat straw, is viewed as a low-cost alternative feed to sugar and starch. It is also potentially available in far greater quantities than sugar and starch feeds. As such, it receives significant attention as a feed material for ethanol production. Like starch, wood and agricultural residues contain polysaccharides. However, unlike starch, while the cellulose fraction of biomass is principally a polymer

of easily fermented C6 sugars, the hemicellulose fraction is principally a polymer of C5 sugars; with quite different characteristics for recovery and fermentation, the cellulose and hemicellulose in biomass are bound together in a complex framework of crystalline organic material known as lignin.

There are several different methods of hydrolysis: (i) concentrated sulfuric acid, (ii) dilute sulfuric acid, (iii) nitric acid, and acid pretreatment followed by enzymatic hydrolysis. The greatest potential for ethanol production from biomass, however, lies in enzymatic hydrolysis of cellulose. The enzyme cellulase, now used in the textile industry to stone wash denim and in detergents, simply replaces the sulfuric acid in the hydrolysis step. The cellulase can be used at lower temperatures, 30 to 50°C, which reduces the degradation of the sugar. In addition, process improvements now allow simultaneous saccharification and fermentation (SSF). In the saccharification and fermentation process, cellulase and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step.

Once the hydrolysis of the cellulose is achieved, the resulting sugars must be fermented to produce ethanol. In addition to glucose, hydrolysis produces other six-carbon sugars from cellulose and five-carbon sugars from hemicellulose that are not readily fermented to ethanol by naturally occurring organisms. They can be converted to ethanol by genetically engineered yeasts that are currently available, but the ethanol yields are not sufficient to make the process economically attractive. It also remains to be seen whether the yeasts can be made hardy enough for production of ethanol on a commercial scale.

The fermentation processes to produce propanol and butanol from cellulose can be difficult to execute, and the *Clostridium acetobutylicum* that is currently used to perform these conversions produces an extremely unpleasant smell, and this must be taken into consideration when designing and locating a fermentation plant. This organism also dies when the butanol content of whatever it is fermenting rises to 7%. For comparison, yeast dies when the ethanol content of its feedstock reaches 14%. Specialized strains can tolerate even greater ethanol concentrations – the so-called turbo yeast can withstand up to 16% ethanol. However, if ordinary *Saccharomyces* yeast can be modified to improve its ethanol resistance, scientists may yet one day produce a strain of the Weizmann organism with a butanol resistance higher than the natural boundary of 7%. This would be useful because butanol has a higher energy density than ethanol, and because waste fiber left over from sugar crops used to make ethanol could be made into butanol, raising the alcohol yield of fuel crops without there being a need for more crops to be planted.

Wet milling and dry milling are the means by which grain and straw fractions are processed into a variety of end products. The processes encompass fermentation and distilling of grains (wheat, rye, or maize). Wet milling starts with water-soaking the grain adding sulphur dioxide to soften the kernels and loosen the hulls, after which it is ground. It uses well-known technologies and allows separation of starch, cellulose, oil, and proteins. Dry milling grinds whole grains (including germ and bran). After grinding, the flour is mixed with water to be treated with liquefying enzymes and, further, cooking the mash to break down the starch. This hydrolysis step can be eliminated by simultaneously adding saccharifying enzymes and fermenting yeast to the fermenter (simultaneous saccharification and fermentation).

After fermentation, the mash (called *beer*) is sent through a multi-column distillation system, followed by concentration, purification, and dehydration of the alcohol. The residue mash (stillage) is separated into a solid (wet grains) and liquid (symp) phase that can be combined and dried to produce distiller's dried grains with soluble constituents, to be used as cattle feed. Its nutritional characteristics and high vegetable fiber content make distiller's dried grains with soluble constituents unsuitable for other animal species.

In separate hydrolysis and fermentation processes, the hydrolysis is carried out in one vessel and the hydrolysate is then fermented in a second reactor. Approximately 73% of the cellulose is converted to ethanol in 48 hr, while the remainder of the cellulose, hemicelluloses, and lignin is burned. The most important parameters are the hydrolysis section yield, product quality, and the required enzyme loading which are all interrelated. Yields are typically higher in more dilute systems where inhibition of enzymes by glucose and cellobiose is minimized. Increasing the amount of enzyme loading can help to overcome inhibition and increase yield and concentration. Increased reaction times also make higher yields and concentrations. Cellulase enzymes from different organisms can result in markedly different performances.

In simultaneous saccharification and fermentation, both the hydrolysis and fermentation are carried out in the same vessel. In this process, yeast ferments the glucose to ethanol as soon as the glucose is produced, preventing

the sugars from accumulating and the end product inhibition. Using the yeast, *Candida brassicae* and the Genencor enzyme (by Genencor International), the yield is increased to 79% and the ethanol concentration produced is 3.7%.

Even in simultaneous saccharification and fermentation, the cellobiose (the soluble sugar) inhibition occurs to an appreciable extent. The hydrolysis is carried out at 37°C (99°F), and increasing the temperature increases the reaction rate; however, the ceiling temperature is limited by the yeast cell viability. The concentration of ethanol is also a limiting factor (This was tested by connecting a flash unit to the SSF reactor and removing the ethanol periodically. This technique showed higher productivities up to 44%). Recycling the residual solids may also increase the process yield. However, the most important limitation in the enzyme recycling comes from the presence of lignin, which is inert to the enzyme. High recycling rates increase the fraction of lignin in the reactor and cause handling difficulties.

In spite of the considerable efforts given to the fermentative alcohols, industrial applications have been delayed because of the high cost of production which depends primarily on the energy input to the purification of dilute end products and on the low productivities of cultures. These two points are linked to inhibition phenomena.

Along with the conventional unit operations, liquid-liquid extraction with biocompatible organic solvents, distillation under vacuum, and selective adsorption on the solids have demonstrated the technical feasibility of the extractive fermentation concept.

Membrane separation processes, which decrease biocompatibility constraints, have been proposed. In fact, the concept of supported liquid membranes has been reported and proposed. This method minimizes the amount of organic solvents involved and permits simultaneous realization of the extraction and recovery phases. Enhanced volumetric productivity and high substrate conversion yields are possible.

See also: Ethanol, Ethanol Production, Fermentation Chemistry, Synthesis – Fermentation.

See also: Fermentation Chemistry, Hydrolysis.

Fermentation Chemistry

The principal components of most plant materials are commonly described as lignocellulosic biomass. This type of biomass is mainly composed of the compounds called cellulose, hemicellulose, and lignin. Cellulose is a primary component of most plant cell walls and is made up of long chains of the 6-carbon sugar, glucose, that are arranged in bundles (often described as crystalline bundles). The cellulose molecules in the plant cell wall are interconnected by another molecule called hemicellulose.

The hemicellulose is primarily composed of the 5-carbon sugar, xylose. Besides cellulose and hemicellulose, another molecule called lignin is also present in significant amounts and provides the structural strength for the plant. Technological developments have recently introduced a variety of processes of extracting and dissolving the cellulose and hemicellulose to produce sugars in such a form that can be readily fermented to ethanol. Generally speaking, appropriate pre-treatment can liberate the cellulose and hemicellulose from the plant material. Further treatment using chemicals, enzymes, or microorganisms can also be applied to liberate simple sugars from the cellulose and hemicellulose, thus making them available to microorganisms for fermentation to ethanol.

The first step in the conversion of sugars to ethanol involves cellulose hydrolysis that is essentially cleaving the chemical bonds in the cellulose to produce glucose.

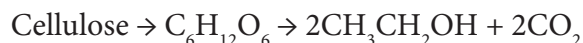
The hydrolysis of cellulose is critical for biofuel production because only glucose, not cellulose, can be consumed by the bacteria used in fermentation to produce biofuel. Cellulose derivatives have crystalline structures due to the dense packing of cellulose chains. They are very stable under many chemical conditions and are not soluble in water, many organic solvents, weak acids, or bases. The crystalline structure can be destroyed and turned into amorphous form under high temperature (>300°C, 570°F) and pressure. There are normally two ways to hydrolyze cellulose: chemically and enzymatically. The chemical method is to use concentrated strong acids to hydrolyze cellulose under high temperature and pressure. However, this method is not preferred by biofuel industry, because toxic by-products remaining in the glucose products will be introduced into the fermentation step, affecting the fermenting bacteria/yeast. Hence, the milder enzymatic method seems to be a much more potential candidate to hydrolyze cellulose.

The enzymatic method uses bacteria-secreted proteins to hydrolyze cellulose which method involves enzymes, such as cellulase. These enzymes play different roles cooperatively in the hydrolysis of cellulose: some cleave the

cellulose chain from the middle into fragments containing 4 to 5 glucose units, some break down these fragments into smaller units of two glucoses, and some finally turn these small units into single glucose unit.

Once the large molecules are extracted from plant cells, they can be broken down into their component sugars using enzymes or acids. The sugars can be subsequently converted to ethanol using appropriately selected microorganisms via fermentation.

The fermentation of ethanol from 6-carbon sugars follows the following stoichiometric equation by which one mole of glucose produces 2 moles of ethanol and 2 moles of carbon dioxide. Thus:



Hemicellulose is made up of the 5-carbon sugar, xylose, arranged in chains with other minor 5-carbon sugars interspersed as side chains. In a similar manner to cellulose, the hemicellulose can also be extracted from the plant material and treated to liberate xylose that, in turn, can be fermented to produce ethanol. However, xylose fermentation is not as straightforward as glucose fermentation. Depending on the microorganism and conditions employed, a number of different fermentation paths are possible and the products can include ethanol, carbon dioxide, and water.

See also: Fermentation.

Fermentation Plants

Traditional fermentation plants producing biogas are in routine use, ranging from farm-size plants to large municipal plants. As feedstock, they use manure, agricultural residues, urban sewage, and waste from households, and the output gas is typically 64% methane.

The biomass conversion process is accomplished by a large number of different agents, from the microbes decomposing and hydrolyzing plant material, over the acidophilic bacteria dissolving the biomass in aquatic solution, and to the strictly anaerobic methane bacteria responsible for the gas formation. Operating a biogas plant for a period of some months usually makes the bacterial composition stabilize in a way suitable for obtaining high conversion efficiency (typically above 60%, the theoretical limit being near 100%), and it is found important not to vary the feedstock compositions abruptly if optimal operation is to be maintained. Operating temperatures for the bacterial processes are only slightly above ambient temperatures, e.g., in the mesophilic region around 30°C (86°F).

See also: Fermentation, Fermentation Chemistry.

Ferrel Cell

The Ferrel cell is operative from 30° latitude to 60° latitude and produces prevailing westerly winds at the surface within these latitudes because some of the air sinking at 30° latitude continues traveling northward toward the poles and the Coriolis force bends it to the right (in the Northern Hemisphere). This air is still warm and at roughly 60° latitude approaches cold air moving down from the poles. With the converging air masses at the surface, the low surface pressure at 60° latitude causes air to rise and form clouds. Some of the rising warm air returns to 30° latitude to complete the Ferrel cell.

The two air masses at 60° latitude do not mix well and form the polar front which separates the warm air from the cold air. Thus, the polar front is the boundary between warm tropical air masses and the colder polar air moving from the north. The polar jet stream aloft is located above the polar front and flows generally from west to east. The polar jet is strongest in the winter because of the greater temperature contrasts than during the summer. Waves along this front can pull the boundary north or south, resulting in local warm and cold fronts which affect the weather at particular locations.

Above 60° latitude, the polar cell circulates cold, polar air equatorward. The air from the poles rises at 60° latitude where the polar cell and Ferrel cell meet, and some of this air returns to the poles completing the polar cell. Because the wind flows from high to low pressure and taking into account the effects of the Coriolis force, the winds above 60° latitude are prevailing easterlies.

In summary, the Ferrel cell is a thermally indirect cell because it is driven by the motions of the cells on either side. At upper levels, the model predicts easterly motion while at the surface, there is a strong belt of surface midlatitude westerlies. However, in reality, upper level westerlies in midlatitudes are observed because at upper levels, there is high pressure in the equator (due to higher temperature) and lower temperature at the poles. Thus, there is a pressure gradient from equator to pole and the actual wind is deflected due to Coriolis, so this causes predominant westerlies at upper levels that are stronger in the winter and, thus, the weather systems migrate from west to east.

See also: Atmosphere, Coriolis Force, Hadley Cell, Polar Cell, Walker Circulation, Wind Energy, Wind Power.

Ferrox Process

Removal of large amounts of hydrogen sulfide from gas streams is accomplished by the Ferrox process. The process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Ferrox process is also used to manage combustion residues in an environmentally safe way at a low cost. Compared to the costs of a traditional cement stabilization, the Ferrox[®]-process has advantages in reducing the overall mass of the residue that has to be disposed combined with a good stabilization.

The process stabilizes the residues, whereby the release of heavy metals and salts is substantially reduced compared to the untreated residues. The process does not yield a new heavy metal-polluted waste stream, but immobilizes the heavy metals in the residue. The salts are extracted from the residues during the process, and the result is a stabilized residue, which is easy to dispose of in an environmentally safe way.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Fibers

Fibers are a class of materials that are continuous filaments or are in discrete elongated pieces, similar to lengths of thread. Natural fibers include those produced by plants, animals, and geological processes and are biodegradable over time. They can be classified according to their origin: (i) vegetable fibers, (ii) wood fibers, (iii) animal fibers, and (iv) mineral fibers.

Vegetable fibers are generally based on arrangements of cellulose, often with lignin: examples include cotton, hemp, jute, and flax. Plant fibers are employed in the manufacture of paper and textile (cloth), and dietary fiber is an important component of human nutrition.

Wood fiber is from tree sources. Forms include groundwood, thermo-mechanical pulp (TMP), and bleached or unbleached kraft or sulfite pulps. Kraft and sulfite, also called sulfite, refer to the type of pulping process used to remove the lignin bonding the original wood structure, thus freeing the fibers for use in paper and engineered wood products such as fiberboard.

Animal fibers consist largely of particular proteins. Examples are spider silk, sinew, catgut, wool, hair such as cashmere, mohair, and angora, and fur such as sheepskin, rabbit, mink, fox, and beaver.

Mineral fibers comprise asbestos, which is the only naturally occurring long mineral fiber. Short, fiber-like minerals include wollastonite, attapulgite, and halloysite.

Fibers are classified by their chemical origin, falling into two groups or families: natural fibers and manufactured fibers. Manufactured fibers are also referred to as man-made or synthetic fibers.

Natural Fibers

Natural fibers are produced by plants and animals, or have a mineral origin: No chemical modification or man-made polymerization process is used to create them, which differentiates them from man-made or synthetic fibers. There are many processing possibilities, e.g., they can be spun into filaments, threads, or ropes, and then they can be woven, knitted, matted, or bound. Plant fibers are mainly composed of cellulose, hemicellulose, and lignin, but also to a minor extent, fats, waxes, pectin, water-soluble substances, and color-carrying substances are included. The shares of these substances vary from fiber to fiber. Also, the indicated properties of natural fibers can have considerable

variations (depending on the growing conditions and the harvesting time, extraction methods, treatment, as well as storage procedures) and will, therefore, serve only as a rough guideline.

Utilization of natural fibers has a long tradition in cultures around the world (e.g., for the production of clothing, building materials, and fishing nets); therefore, people who deal with traditional fiber types do not necessarily tend to refer to the relatively new term “biorefinery.” However, the possibilities of sustainably using several plant parts (seeds, lignocellulose parts of lower value) for various purposes, replacing less sustainable products (such as fossil-resource-based materials) and increasing regional added-value bring natural fibers into the limelight again in the context of the discussion of building a biobased economy. Regarding technical applications, the largest share of natural fibers is still used for traditional applications such as yarns, twines, and clothes; other applications are pulp and paper (especially specialty papers), composites (e.g., for the automotive industry), geo- and agro textiles, insulation products, and by-product utilization (e.g., animal bedding, construction material, gardening and boards), and for the purpose of energy.

Man-made Fibers

Man-made fibers are either significantly modified natural fibers (so-called regenerates, mostly cellulose), mineral (inorganic) man-made fibers, or synthetic fibers (man-made monomers are polymerized and processed into fibers). Man-made fibers, such as nylon, polyester, and rayon, are produced by chemical reactions controlled by people, rather than occurring naturally. The term synthetic fibers is often used to designate man-made fibers; however, to many people, this term has a negative connotation, meaning inauthentic, artificial, or fake.

Man-made cellulose fibers, in contrast to natural fibers, are not defined by a single feedstock (e.g., viscose can be produced from wood as well as from cotton linter). The characterization of these fibers depends on the production processes used and the final fiber properties. Important man-made cellulose-based fibers include Viscose, Modal, Lyocell, and acetate fibers, which can be produced as staple or as filament fibers. The main source of man-made cellulosic fibers is wood. A variety of processes is available to separate the cellulosic wood fibers, which are often followed by different bleaching procedures.

Fiber products are products derived from fibers of herbaceous and woody plant materials; examples include pulp, composition board products, and wood chips for export.

See also: Fiber.

Filters

Filters can be used to remove particles from liquid streams and from gas streams. Pressure filters are generally automatic devices in which the contaminated water is sucked inwards through a series of leaves on which a filter cake forms.

The filtration process involves a filter medium, over which water flows. This filter media blocks passage of contaminants through physical obstruction, chemical adsorption, or a combination of both processes. Material construction of the filter media varies widely, but the most effective media are made from carbon or a combination of carbon with other elements. Generally, water goes through several stages of filtration to ensure that each filter media will remove the ultimate number of contaminants. Water normally passes through a water filter at a relatively low speed, in order to ensure adequate contact time with the filter media. Once the water has passed through the required stages of filtration, it emerges as pure drinking water, free from contamination.

The filter may be used to remove particles from shale oil retort waters as the first stage in a treatment system, or it can be used to dewater the sludge products from other separators. The filter cake is generally low in moisture, which eases disposal problems. Vacuum filtration can also be used to remove suspended particles from wastewater but is more suitable for dewatering concentrated streams and sludge. In the rotary vacuum filter, a rotating drum dips into a trough filled with wastewater, and suction is applied to the inside of the drum. Water is drawn through the perforated surface of the drum, and solids are deposited on the outside as a filter cake. As the drum rotates, the dewatered sludge is scraped off and falls into a receiving trough. A filter press is functionally similar except that the wastewater is sucked or pumped through a series of plate-and-frame assemblies. The dewatered sludge is periodically removed from the filter medium by mechanical cleaning.

Ultrafiltration, in which the wastewater is forced through a membrane, is often used for separation of oil and water. It is generally limited to separation of chemically stabilized emulsions and is not suitable for mechanical emulsions. In multimedia filters, granular materials such as sand form a filtering bed through which the wastewater is pumped. The water passes through a series of layers with granules of increasingly fine size. The collected solids are subsequently removed by back-flushing with clean water. This filter produces sludge, rather than a dry cake, which requires additional dewatering before disposal. The multimedia filter is generally more economical than pressure filters for high flow rates and dilute slurries.

See also: Fabric Filter, Gas Cleaning, Gas Processing, Gas Treating.

Filter Tubes

At some stage of gas processing, the gas flow is directed to a unit that contains a series of filter tubes. As the velocity of the stream reduces in the unit, primary separation of remaining contaminants occurs due to gravity. Separation of smaller particles occurs as gas flows through the tubes, where they combine into larger particles which flow to the lower section of the unit. Further, as the gas stream continues through the series of tubes, a centrifugal force is generated which further removes any remaining water and small solid particulate matter.

See also: Fabric Filter, Filters, Filtration, Gas Cleaning, Gas Processing, Gas Treating.

Filtration

Filtration is a mechanical or physical operation which is used for the separation of solids or small particles from fluids (liquids or gases) by interposing a medium to fluid flow through which the fluid can pass, but the solids (or at least part of the solids) in the fluid are retained. It has to be emphasized that the separation is NOT complete, and it will depend on the pore size and the thickness of the medium as well as the mechanisms that occur during filtration.

The filtration process separates particles and fluid from a suspension, and the fluid can be either a liquid or a gas (or a supercritical fluid). To separate a mixture of chemical compounds, a solvent is chosen which dissolves one component, while not dissolving the other. By dissolving the mixture in the chosen solvent, one component will go into the solution and pass through the filter, while the other will be retained. Filtration also cleans up air streams or other gas streams. Furnaces use filtration to prevent the furnace elements from fouling with particulates. Pneumatic conveying systems often employ filtration to stop or slow the flow of material that is transported, through the use of a baghouse.

Filtration processes can be subdivided into three broad categories: (i) cake filtration, (ii) depth filtration, and (iii) surface filtration. In cake filtration, the porous barrier holds back the solid particles, which build up into a steadily thickening cake as the filtration progresses. However, the cake must be sufficient to allow the fluid to flow through it as the cake builds up. In depth filtration, the porous barrier is a relatively thick layer of coarse material. This allows clear fluid to pass through while trapping the solid particles in the relatively coarse spaces between the particles forming the filter bed. In surface filtration, the porous barrier is a membrane of controlled pore size. The solid particles are stopped if they are too large to pass through the pores in the barrier. Thus, the filtration in this case is essentially a straining process, much like screening. However, because the filtration barrier tends to blind (that is, plug) the pores with solid particles, the filtration rate decreases as the filtration progresses and the filter is completely plugged before a cake can be formed.

There are two main types of filter media: (i) a solid sieve which traps the solid particles, with or without the aid of filter paper, and (ii) a bed of granular material which retains the solid particles as it passes. The first type allows the solid particles, i.e., the residue, to be collected intact; the second type does not permit this. However, the second type is less prone to clogging due to the greater surface area where the particles can be trapped. Also, when the solid particles are fine, it is often more economic and easier to discard the contaminated granules than to clean the solid sieve.

Filtration is a more efficient method for the separation of mixtures than decantation, but is much more time consuming. If small amounts of solution are involved, most of the solution may be soaked up by the filter medium.

An alternative to filtration is centrifugation in which a mixture of solid and liquid particles is centrifuged to force the (usually) denser solid to the bottom, where it often forms a firm cake. The liquid above can then be decanted.

See also: Fabric Filter, Filters, Filter Tubes, Gas Cleaning, Gas Processing, Gas Treating.

Fire Point and Flash Point

The *fire point* is the temperature to which the gas must be heated under the prescribed conditions of the test method to burn continuously when the mixture of vapor and air is ignited by a specified flame (ASTM D92).

Flash point is the temperature at which the ignition source will ignite the testing sample. The flash point is determined by heating the sample of fuel in a container and passing the flame over the surface of the sample. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed. The flash produced need not be sustained for a long time. Whereas the fire point is the minimum temperature at which the vapor of the fuel steadily burns at least for five seconds once ignited. Flash point and fire point are the property that directly signifies whether the fuel is safely transportable; it is not related to engine performance.

From the viewpoint of safety, information related to the flash point is of most significance at or slightly above the maximum temperatures (30 to 60°C, 86 to 140°F) that may be encountered in storage, transportation, and use of liquid crude oil products, in either closed or open containers. In this temperature range, the relative fire and explosion hazard can be estimated from the flash point. For products with flash point below 40°C (104°F), special precautions are necessary for safe handling. Flash points above 60°C (140°F) gradually lose their safety significance until they become indirect measures of some other quality.

The fire point and the flash depend upon the volatility of the fuel – volatility is the tendency of the substance to vaporize, and it is related to the vapor pressure of the fuel at that particular temperature. The fuel exhibiting higher vapor pressure at a given temperature is said to be more volatile than the one exhibiting lower vapor pressure at the same temperature. Hence, the lower the normal boiling point, the higher the volatility, which is in turn inversely proportional to its fire point and the flash.

See also: Flammability Range Flash Point, Volatility, Flammability, and Explosive Properties.

Firewood

Firewood is any wood designated for, and used as, fuel but often refers to trees cut for that purpose. Seasoned firewood contains approximately 20% to 25% w/w moisture, compared to freshly cut or green wood, which can contain approximately 45% w/w moisture – green wood that has been recently cut and therefore has not had an opportunity to season (dry) by evaporation of the internal moisture. Softwood reaches good seasoning in six to twelve months, while hardwood takes longer. During this time, whether the wood rests on the forest floor or sits stacked and stored at a domestic location, wind and sun work to evaporate excess moisture.

Wood contains microscopic tubes that carry water from the roots through the tree. When a tree falls, water transportation ceases, but moisture remains. This moisture must evaporate to give you the best wood to burn. If you try to burn green wood, the heat produced will first attempt to dry the wood and then put any remaining energy into actually burning it, resulting in minimal heat output and increased creosote buildup in the chimney and flue.

When considering the type of wood for use as firewood, several characteristics are important. These include properties such as heat value, ease of splitting, weight per unit volume, ease of starting, and the amount of smoke produced. The moisture content of the wood, number of knots, and pitch content affect these characteristics of the more common woods used as firewood.

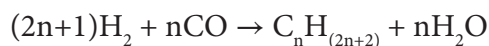
All woods dried to the same moisture content contain approximately the same heat value per pound which is on the order of 8,000 to 9,500 Btu for fully dried wood and 5,500 to 8,500 Btu for air-seasoned wood. However, the heat content of any fire depends on wood density, resin, ash, and moisture. Generally, one cord of well-seasoned hardwood (measuring 8 feet long, 4 feet high, and 4 feet wide or 128 cubic feet and weighing approximately two tons) burned in an airtight, draft-controlled wood stove with a 55 to 65% efficiency is equivalent to approximately 175 gallons of #2 fuel oil or 225 therms of natural gas consumed in a typical normal furnace having a 65 to 75% efficiency.

Forest biomass or agricultural residues are almost completely comprised of lignocellulosic molecules (wood), a structural matrix that gives the tree or plant strength and form. This type of biomass is a prime feedstock for combustion, and indeed remains a major source of energy in many parts of the world. The thermochemical platform utilizes pyrolysis and gasification processes to recover heat energy as well as the gaseous components of wood, known as synthesis gas or syngas. The synthesis gas can then be refined into synthetic fuels, including Fischer-Tropsch, methanol, and ethanol, through the process of catalytic conversion.

See also: Cord, Cordwood, Wood.

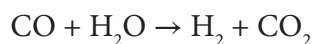
Fischer-Tropsch Process

The Fischer-Tropsch process is a catalytic chemical reaction in which carbon monoxide (CO) and hydrogen (H₂) in the synthesis are converted into hydrocarbon derivatives of various molecular weights. The synthesis gas that is required as the feedstock for the Fischer-Tropsch process is typically produced by gasification of coal, crude oil resid, biomass, organic waste, or by various reforming processes. The process can be represented by the simple equation:



In this equation, n is an integer. Thus, for $n = 1$, the reaction represents the formation of methane, which in most gas-to-liquid (GTL) applications is considered an undesirable by-product.

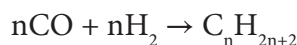
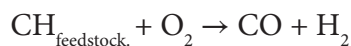
The Fischer-Tropsch process conditions are usually chosen to maximize the formation of higher molecular weight hydrocarbon liquid fuels which are higher value products. There are other side reactions taking place in the process, among which the water-gas-shift reaction is predominant:



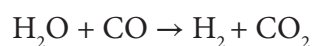
Depending on the catalyst, temperature, and type of process employed, hydrocarbon derivatives ranging from methane to higher molecular paraffin derivatives and olefin derivatives can be obtained. Small amounts of low molecular weight oxygenated derivatives (such as alcohol derivatives and organic acid derivatives) are also formed. Typically, Fischer-Tropsch liquids are (unless the process is designed for the production of other products) hydrocarbon products (which vary from naphtha-type liquids to wax) and non-hydrocarbon products. The production of non-hydrocarbon products requires adjustment of the feedstock composition and the process parameters.

Briefly, synthesis gas is the name given to a gas mixture that contains varying amounts of carbon monoxide (CO) and hydrogen (H₂) generated by the gasification of a carbonaceous material. Examples include steam reforming of natural gas, crude oil residua, coal, and biomass. Synthesis gas is used as an intermediate in producing hydrocarbon derivatives via the Fischer-Tropsch for use as gaseous and liquid fuels.

The synthesis gas is produced by the gasification conversion of carbonaceous feedstock such as crude oil residua, coal, and biomass, and production of hydrocarbon products can be represented simply as:



However, before conversion of the carbon monoxide and hydrogen to hydrocarbon products, several reactions are employed to adjust the hydrogen/carbon monoxide ratio. Most important is the water gas shift reaction in which additional hydrogen is produced (at the expense of carbon monoxide) to satisfy the hydrogen/carbon monoxide ratio necessary for the production of hydrocarbon derivatives:



The boiling range of Fischer-Tropsch typically spans the naphtha and kerogen boiling ranges and are suitable for analysis by application of the standard test methods. With the suitable choice of a catalyst, the preference for products boiling in the naphtha range (<200°C, <390°F) or for product boiling in the diesel range (approximately 150 to 300°C, 300 to 570°F) can be realized.

Fischer-Tropsch Process – Catalysts

In the Fischer-Tropsch process, the temperature, pressure, and the catalyst type determines the chain polymerization versus chain termination ratio. This ratio governs the average molecular weight of the hydrocarbon mixture (syn-crude, synthetic crude oil) produced.

In fact, there is either a low temperature Fischer-Tropsch process (LTFT) or high temperature Fischer-Tropsch process (HTFT): (i) the low-temperature Fischer-Tropsch process operates at 200 to 240°C (390 to 465°F), and typically, an iron or cobalt catalyst is employed, and (ii) the high-temperature Fischer-Tropsch process operates HTFT: 300 to 350°C (570 to 660°F), and typically, an iron catalyst is employed. An increase in temperature leads to shorter chains (except at 330°C/625°F); mostly gasoline and olefins are produced; at 180 to 250°C (355 to 480°F) when mostly diesel and waxes are produced.

Several types of catalysts can be used for the Fischer-Tropsch synthesis. The most important catalysts are based on iron (Fe) or cobalt (Co). Cobalt catalysts have the advantage of a higher conversion rate and a longer life (over five years). The cobalt catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbon derivatives and alcohols compared to iron catalysts. Iron catalysts have a higher tolerance for sulfur, are cheaper, and produce more olefin products and alcohols. The lifetime of the iron catalysts is short and in some commercial installations, may be measured in weeks.

Nickel oxide catalysts have high activity, are more selective toward shorter chains and will tend to the production of methane, and do not do well at higher pressures. Cobalt oxide is much more resistant to oxidation by oxygen and water giving it a higher activity and longer life than iron. Ruthenium catalysts favor selectivity of the gasoline and jet fuel- C₉-C₁₆ hydrocarbon derivatives using a supported zeolite matrix.

Manganese has been widely used as one of the promoters for the Fischer-Tropsch process on iron catalyst, particularly in producing low olefins. Efforts have also been exerted on the individual effect of manganese promotion on supported or unsupported iron catalysts. Iron-manganese (Fe-Mn) and cobalt-manganese (Co-Mn) catalysts favor the production of ethylene and butylenes and high yields for these olefins has been correlated with the iron manganese oxides phase and two carbide phases, while the manganese-rich solid has been correlated with two spinel phases and different carbide phases.

The iron-manganese catalyst, as one of the most important catalyst systems, has received extensive attention in recent years because of the higher olefin and middle distillation cut selectivity which allows their products to be used as a feedstock for the chemical industry. Therefore, the iron-manganese catalyst has a promising industrial application, and it is well known that higher selectivity of alkene derivatives can be obtained on iron-manganese catalysts than on other iron-based catalysts.

See also: Fischer-Tropsch, Fischer-Tropsch Process, Synthesis Gas.

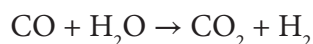
Fischer-Tropsch Chemicals

Fischer-Tropsch chemicals are the products of the Fischer-Tropsch reaction in which synthesis gas (a mixture of carbon monoxide and hydrogen) is reacted to produce hydrocarbon derivatives and oxygenated species such as alcohols and ketones. The synthesis of hydrocarbon derivatives from synthesis gas (the Fischer-Tropsch synthesis) is a procedure for the indirect liquefaction of carbonaceous feedstocks.

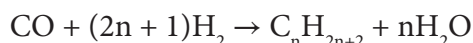
The production of synthesis gas (syngas) involves the reaction of carbonaceous feedstock with steam and oxygen; the gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products. In addition, synthesis gas may also be used to produce a variety of products, including methanol.

Gasification may be attained by means of any one of several processes or even by gasification of the carbonaceous feedstock in place (underground gasification, in situ gasification). The exothermic nature of the process and the decrease in the total gas volume in going from reactants to products suggest the most suitable experimental conditions to use in order to maximize product yields.

In practice, the Fischer-Tropsch reaction is carried out at temperatures of 200 to 350°C (390 to 660°F) and at pressures of 75 to 4,000 psi; the hydrogen/carbon monoxide ratio is usually approximately 2.2:1 or 2.5:1. Since up to three volumes of hydrogen may be required to achieve the next stage of the liquids production, the synthesis gas must then be converted (by means of the water-gas shift reaction) to the desired level of hydrogen:



The gaseous mix is purified (for example, acid gas removal) and converted to a wide variety of hydrocarbon derivatives:



These reactions result primarily in low-boiling and medium-boiling range aliphatic compounds such as n-hydrocarbon derivatives as olefins and oxygenated products.

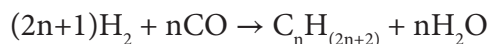
See also: Gasifiers, Gasification.

Fischer-Tropsch Process

In addition to carbonaceous feedstock and gas streams, biomass can also be used as a gasification feedstock to provide synthesis gas for the Fischer-Tropsch production of hydrocarbon derivatives and/or methanol. There are two routes for the production of synthetic fuels from gas streams (via synthesis gas) which are (i) the hydrocarbon derivatives route and (ii) the methanol route. Both routes often fall under the general umbrella description of the Fischer-Tropsch synthesis.

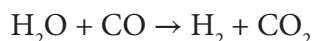
The Fischer-Tropsch process (or Fischer-Tropsch synthesis) is a catalyzed chemical reaction in which synthesis gas, a mixture of carbon monoxide and hydrogen, is converted into liquid hydrocarbon derivatives of various forms. The most common catalysts are based on iron and cobalt, although nickel and ruthenium have also been used. The principal purpose of this process is to produce a synthetic crude oil substitute from a carbonaceous feedstock for use as synthetic lubrication oil or as synthetic fuel. In fact, the combination of biomass gasification and Fischer-Tropsch synthesis is a possible route to produce renewable transportation fuels (biofuels).

The Fischer-Tropsch process involves a variety of competing chemical reactions, which lead to a series of desirable products and undesirable by-products. The most important reactions are those resulting in the formation of alkanes:

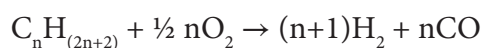


The process parameters and the catalyst composition are usually chosen, so as to favor higher order reactions ($n > 1$) and thus minimize methane formation. Most of the alkanes produced tend to be straight-chained, although some branched alkanes are also formed. In addition to alkane formation, competing reactions result in the formation of alkenes, as well as alcohols and other oxygenated hydrocarbon derivatives.

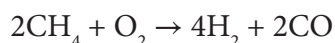
An important aspect of the Fischer-Tropsch process is the water-gas-shift reaction:



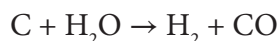
This reaction can be used to shift the hydrogen/carbon monoxide ratio of the synthesis gas. The initial reactants for the Fischer-Tropsch process (i.e., CO and H_2) can be produced by other reactions such as the partial combustion of a hydrocarbon:



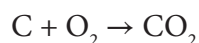
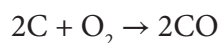
For example (when $n = 1$), methane (in the case of gas-to-liquid applications):



Or by the gasification of biomass:



The energy needed for this endothermic reaction of carbonaceous materials (such as biomass and solid waste) and steam is usually provided by (exothermic) combustion with air or oxygen:



Generally, the Fischer-Tropsch process is operated in the temperature range of 150 to 300°C (300 to 570°F). Higher temperatures lead to faster reactions and higher conversion rates, but also tend to favor methane production. As a result, the temperature is usually maintained at the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes, both of which are desirable. Typical pressures are in the range of one to several tens of atmospheres. Chemically, even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment.

A variety of synthesis gas compositions can be used. For cobalt-based catalysts, the optimal hydrogen/carbon monoxide ratio is approximately 1.8-2.1. Iron-based catalysts promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This can be important for synthesis gas derived from biomass, which tends to have relatively low hydrogen/carbon monoxide ratios (<1).

In general, the product distribution of hydrocarbon derivatives formed during the Fischer-Tropsch process follows an Anderson-Schulz-Flory distribution:

$$W_n/n = (1-\alpha)^2 \alpha^{n-1}$$

A variety of catalysts can be used for the process – the most common catalysts are based on iron and cobalt, although nickel and ruthenium have also been used.

Cobalt seems to be the most active catalyst, although iron also performs well and can be more suitable for low-hydrogen-content synthesis gases such as those derived due to the promotion of the water-gas-shift reaction. Nickel can also be used, but tends to favor methane formation. In addition to the active metal, the catalysts typically contain a number of promoters, including potassium and copper, as well as high-surface-area binders/supports such as silica, alumina, or zeolites.

Thus, cobalt-based catalysts are preferred for Fischer-Tropsch synthesis when the feedstock is natural gas due to the higher activity of the cobalt catalyst. Natural gas has a high hydrogen-to-carbon ratio, so the water-gas-shift is not needed for cobalt catalysts. Iron catalysts are preferred for lower-quality feedstocks such as biomass. Iron catalysts are also susceptible to sulfur poisoning, but the lower cost of iron makes sacrificial catalyst at the front of a reactor bed economical. Iron can also catalyze the water-gas-shift to increase the hydrogen-to-carbon ratio to make the reaction more favorably selective. However, Fischer-Tropsch catalysts are notoriously sensitive to the presence of sulfur-containing compounds, and the sensitivity of the catalyst to sulfur is higher for cobalt-based catalysts than for their iron counterparts.

The Fischer-Tropsch product spectrum consists of a complex multi-component mixture of linear and branched hydrocarbon derivatives and oxygenated products. The main products are linear paraffins and α -olefins. The hydrocarbon synthesis is catalyzed by metals such as cobalt, iron, and ruthenium. Both iron and cobalt are used commercially at a temperature of 200 to 300°C (390 to 570°F) and at 150 to 900 psi.

See also: Biomass, ExxonMobil AGC-21 Process, Fischer-Tropsch Process, Fischer-Tropsch Process – Catalysts, Fischer-Tropsch Process – Chemicals, Fischer-Tropsch Process – Chemistry, Fischer-Tropsch Process – Commercial Processes, Fischer-Tropsch Process – Process Chemistry, Fischer-Tropsch Process – Products, Fischer-Tropsch Process – Product Separation and Upgrading, Fischer-Tropsch Process – Reactors.

Fischer-Tropsch Process – Chemistry

In the Fischer-Tropsch synthesis, hydrocarbon derivatives (C_xH_y) are synthesized from carbon monoxide (CO) and hydrogen (H_2) (synthesis gas, syngas). The Fischer-Tropsch process is an established technology and already applied on a large scale.

The number of chemical reactions involved in the manufacture of synthesis gas is large. The most important of these (limited to methane since it is the major constituents of natural gas) and given the objective of producing carbon monoxide and hydrogen from the methane, the most desirable reactions are those of reforming (Reaction 1) and partial oxidation (Reaction 3) producing hydrogen/carbon monoxide ratios of 3 and 2, respectively. If a source of carbon dioxide is available (or for gas streams rich in carbon dioxide) reforming with carbon dioxide (Reaction 2) provides a hydrogen/carbon monoxide ratio of 1. The data for higher molecular weight (higher boiling) hydrocarbon derivatives in some gas streams are correspondingly lower. The final hydrogen/carbon monoxide ratio is influenced further by the carbon monoxide shift reaction (Reaction 5).

Reforming (strongly endothermic):



Combustion (strongly exothermic):



Shift conversion (mildly exothermic):

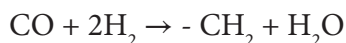


Carbon formation:

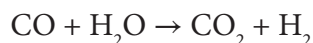


The reforming reactions (1 and 2) are strongly endothermic and must be supported by the strongly exothermic reactions of partial oxidation (3) and/or complete combustion (4). The latter reaction is, however, in principle less desirable since neither hydrogen nor carbon monoxide is produced.

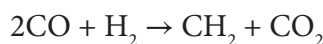
Thus, in the (exothermic) Fischer-Tropsch reaction, one mole of carbon monoxide reacts with two moles of hydrogen to afford a hydrocarbon chain extension ($-CH_2-$). The oxygen from the CO is released as product water:



The reaction implies a hydrogen-carbon monoxide ratio of at least 2 for the synthesis of the hydrocarbon derivatives. When the ratio is lower, it can be adjusted in the reactor with the catalytic water-gas-shift reaction:



When catalysts with water-gas-shift activity are used, the water produced in the reaction can react with carbon monoxide to form additional hydrogen. In this case, a minimal hydrogen-to-carbon monoxide (H_2/CO) ratio of 0.7 is required and the oxygen from the carbon monoxide is released as carbon dioxide:



The reaction affords mainly aliphatic straight-chain hydrocarbon derivatives (C_xH_y). Besides these straight-chain hydrocarbon derivatives, also, branched hydrocarbon derivatives, unsaturated hydrocarbon derivatives (olefins), and primary alcohols are formed in minor quantities. The kind of liquid obtained is determined by the process parameters (temperature, pressure), the kind of reactor, and the catalyst used. Typical operation conditions for the Fischer-Tropsch synthesis are a temperature range of 200 to 350°C (390 to 660°F) and pressures of 220 to 590 psi, depending on the process.

The Fischer-Tropsch process is a complicated process that requires a well-defined choice of reactors, catalysts, and operating conditions to synthesize the desired products. Even then, a mixture of compounds is obtained. The Fischer-Tropsch synthesis was originally operated in packed bed reactors. These reactors have several drawbacks that can be overcome by a slurry reactor. In these slurry reactors, the synthesis gas is bubbled through a suspension of catalyst particles (typically 30 to 50 micrometers) in an inert liquid. The heat of reaction is removed by circulating the slurry through external or internal heat exchangers. The slurry reactor can be operated at higher temperatures and at low H_2/CO ratios without problems due to efficient heat transfer and uniform temperatures. The application of small catalyst particles caused no occurrence of intra-particle heat and mass transfer resistances.

The Fischer-Tropsch synthesis in a slurry bubble column has several advantages over the fixed bed reactors. Because the Fischer-Tropsch process offers a number of advantages in slurry phase over the two-phase processes, special attention is paid to the effects of an inert liquid phase on the reaction rate, mass transfer, and product distribution.

See also: Fischer-Tropsch, Fischer-Tropsch Process, Synthesis Gas.

Fischer-Tropsch Process – Commercial Processes

The three main industrially proven processes involve various versions of tubular steam reforming, catalytic auto-thermal reforming, and non-catalytic partial oxidation.

In tubular steam reforming, the methane-steam reaction (reaction 1, above) takes place over a catalyst in a tube that is externally heated. A large steam surplus is required to suppress carbon formation in the catalyst. This tends to drive the carbon monoxide-steam shift reaction (reaction 5, above) to the right resulting in a hydrogen-rich synthesis gas. The heat is supplied largely by the undesirable complete combustion reaction of methane to carbon dioxide and water (reaction 4, above) outside of the tubes.

In catalytic auto-thermal reforming, oxygen is added to the feed. The heat requirement for the methane-steam reaction (reaction 1, above) is largely met by the methane-oxygen partial oxidation reaction (reaction 3, above) thus producing a lower hydrogen/carbon monoxide ratio in the synthesis gas. As in tubular reforming, considerable amounts of steam are required to suppress carbon formation. The absence of the metallurgical limitations of the catalyst tubes of a steam reformer allows higher operating temperatures thus reducing methane slip. At these higher temperatures, the carbon monoxide shift equilibrium is also more favorable to carbon monoxide than in the case of the tubular steam reformer.

In non-catalytic partial oxidation, the reaction of methane with oxygen (reaction 3, above) is dominant. The absence of any catalyst means that the process is tolerant of a small degree of carbon formation and allows even

higher operating temperatures. It is thus possible to operate partial oxidation without any steam addition, and the resulting synthesis gas is rich in carbon monoxide.

The art of selecting the most appropriate process (or a combination of processes) for synthesis gas generation consists of ensuring the correct gas specification as required by the selected synthesis while simultaneously minimizing certain inherent inefficiencies of the individual processes. In the case of tubular reforming, this inherent inefficiency lies in the use of external complete combustion requiring an expensive heat recovery train and still involving substantial losses in the stack gas. In the case of auto-thermal reforming and partial oxidation, the inefficiency lies in the energy requirement and investment for the oxygen plant.

The Synthol process has been operated at commercial scale since the 1950s by Sasol, and has undergone some evolution. The initial process, the Arge Process, involved low temperatures (200 to 250°C, 390 to 480°F), medium pressures, and a fixed catalyst bed. The process primarily produced a linear paraffin wax, which had use as petrochemical feedstock and also for transport fuels after further processing. This was the only process available until the 1950s/1960s when the Sasol Synthol process was developed and the process involved higher temperatures (300 to 360°C, 570 to 680°F) and medium pressures, but used a circulating fluidized bed to produce low-boiling olefin derivatives for chemicals production and gasoline components. This process has recently been updated to the Advanced Synthol process.

The latest development of Fischer-Tropsch technology is the Sasol slurry phase reactor, which is an integral part of the Sasol slurry phase distillate (SSPD) process, and carries out the synthesis reaction at low temperatures (200 to 250°C, 390 to 480°F) and low pressures.

The process involves bubbling hot synthesis gas through a liquid slurry of catalyst particles and liquid reaction products. Heat is removed from the reactor via coils within the bed producing steam. Liquid products are removed from the reactor, and the liquid hydrocarbon wax is separated from the catalyst. The gas stream from the top of the reactor is cooled to recover low-boiling hydrocarbon derivatives and reaction water. The Sasol slurry phase technology has undergone several developments primarily concerned with catalyst formulations. The initial development used an iron-based catalyst, but recent developments have used a cobalt-based catalyst, giving greater conversion.

The Shell middle distillate synthesis (SMDS) process is a two-step process that involves Fischer-Tropsch synthesis of paraffinic wax called the high-boiling paraffin synthesis (HPS). The wax is subsequently hydrocracked and isomerized (in the presence of hydrogen) to yield a middle distillate boiling range product in the high-boiling paraffin conversion.

In the high-boiling paraffin synthesis stage, wax is maximized by using a proprietary catalyst having high selectivity toward heavier products and by the use of a tubular, fixed-bed reactor. The high-boiling paraffin conversion stage employs a commercial hydrocracking catalyst in a trickle flow reactor. The high-boiling paraffin conversion step allows for production of narrow range hydrocarbon derivatives not possible with conventional Fischer-Tropsch technology.

The products manufactured are predominantly paraffinic, free from sulfur, nitrogen, and other impurities, and have excellent combustion properties. The high cetane number and smoke point indicate clean-burning hydrocarbon liquids having reduced harmful exhaust emissions. The process can also be proposed to produce chemical intermediates, paraffinic solvents, and extra high viscosity index lube oils.

The Lurgi combined reforming process was originally developed for large-scale methanol production, and it is with an example from this application that is described here. In the context of the production of liquid fuels, it is suitable as a building block for the methanol-to-gasoline (MTG) process or the olefins-to-gasoline, and distillates (MOGD) process. For the high-pressure Synthol process, carbon dioxide needs to be purged from the system. The conventional tubular steam reforming process as used for synthesis gas production produces a hydrogen/carbon monoxide ratio of over 4 and a stoichiometric ratio of 2.6 to 2.9 (i.e., a hydrogen-rich gas) depending on the quality of the feedstock gas stream.

Auto-thermal reforming or partial oxidation produces carbon monoxide-rich gases with a hydrogen/carbon monoxide ratio in the range 1.5 to 3.5 and a stoichiometric number of approximately around 1.8.

Approximately half the feed is processed in the tubular primary reformer. The other half, together with the primary reformer effluent, is auto-thermally reformed with pure oxygen in the secondary reformer. Besides matching hydrogen-rich and carbon monoxide-rich process steps to produce an optimum stoichiometric ratio, the Combined Reforming process has beneficial effects such as:

The methane slip of the overall reforming process is governed by the temperature of the secondary reformer that is not subject to the same limitations of tube metallurgy as the tubular reformer. The combined process can thus provide a lower methane slip. Less synthesis gas of the optimized quality is required per ton of methanol, reducing both the synthesis gas compressor load and the capital cost of the synthesis unit.

The operating temperature of the primary reformer need no longer be chosen to minimize methane slip. The reformer can be operated under mild conditions. The higher operating pressure thus possibly enables the synthesis gas compressor load to be further reduced.

The reduced throughput through the primary reformer together with the lower operating temperature combine to reduce the tubular reformer to approximately 25% of the size of that required for the single stage process. This reduces the stack gas losses referred to earlier by the same amount.

One feature common to all Fischer-Tropsch processes is the inherent lack of selectivity. The actual selectivity will depend on the desired product slate as well as on the catalyst and the operating conditions. In all cases, however, substantial quantities of gaseous hydrocarbon derivatives including methane are produced.

In principle, it is desirable to recycle these gaseous hydrocarbon derivatives to produce more synthesis gas. On the other hand, it is necessary to provide a purge of inert gases, principally argon and nitrogen. The other aspect of selectivity that requires recognition is that a proportion of higher molecular weight products, including waxes, is produced and may require hydrotreating for conversion to a saleable product.

The Syntroleum process is a cost-effective refinement of gas-to-liquid technology that has been in use for several decades. A major advantage is that the process uses compressed air instead of pure oxygen to facilitate the conversion reaction, substantially reducing the capital costs and vastly improving the safety of the process plants.

See: ExxonMobil AGC-21 Process, Fischer-Tropsch, Fischer-Tropsch Process, Synthesis Gas.

Fischer-Tropsch Process – Products

The subsequent chain-growth in the Fischer-Tropsch process is comparable with a polymerization process resulting in a distribution of chain-lengths of the products (Table F-4). In general, the product range includes the low-boiling hydrocarbon derivatives methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}), naphtha (C_5H_{12} to $\text{C}_{12}\text{H}_{26}$), kerosene-diesel fuel ($\text{C}_{13}\text{H}_{28}$ to $\text{C}_{22}\text{H}_{46}$), low molecular weight wax ($\text{C}_{23}\text{H}_{48}$ to $\text{C}_{32}\text{H}_{66}$), and high molecular weight wax ($>\text{C}_{33}\text{H}_{68}$). Linear alpha-olefins are also produced, but the distribution of the products depends on the catalyst and the process operation conditions (temperature, pressure, and residence time).

Table F-4 Range of Potential Fischer-Tropsch Products.

Carbon number	Product
C1-C2	Synthetic natural gas (SNG) Petrochemical feedstock
C3-C4	Liquefied petroleum gas (LPG) Petrochemical feedstock
C5-C7	Low-boiling naphtha
C8-C10	High-boiling naphtha
C11-C20	Middle distillate
C11-C12	Low-boiling kerosene
C13-C20	High-boiling kerosene
C21-C30	Soft wax
C31-C60	Hard wax

The (theoretical) chain length distribution can be described by means of the Anderson-Schulz-Flory equation:

$$\text{Log } W_n/n = 2 \log (\ln \alpha) + n \log \alpha$$

W_n is the weight fraction of chains with n carbon atoms and the chain growth probability factor (α) that is defined by:

$$\alpha = k_p/k_p + k_t$$

In this equation, k_p is the propagation rate and k_t is the termination rate.

See also: Fischer-Tropsch, Fischer-Tropsch Process, Fischer-Tropsch Chemistry, Fischer-Tropsch Commercial Processes, Synthesis Gas.

Fischer-Tropsch Process – Product Separation and Upgrading

Conventional refinery processes can be used for upgrading of Fischer-Tropsch liquid and wax products. There are currently two well-defined routes of Fischer-Tropsch synthesis: (i) a low temperature process and (ii) a high temperature process. The first is employed in the production of waxes, which are converted into naphtha or diesel oil after the hydroprocessing. The second is employed in the production of gasoline and alpha-olefins. Fuels produced with the Fischer-Tropsch synthesis are of a high quality due to a low aromaticity and zero sulfur content.

The product stream consists of various fuel types which are (i) liquefied petroleum gas, LPG, (ii) gasoline, (iii) diesel fuel, and (iv) jet fuel as well as other products. Hydroprocessing is employed in the treatment of wax produced at a low temperature. The wax is basically composed of linear paraffin and small quantities of olefins and oxygenates. The hydrogenation of the olefins and the oxygenated compounds, besides hydrocracking of wax, can be conducted in conditions that are not very severe, with the production of naphtha and diesel oil.

Upgrading Fischer-Tropsch products is necessary for the conversion of heavier waxes into usable and lower-boiling products in the kerosene boiling range. Product upgrading is an optional stage added to the Fischer-Tropsch synthesis of gas-to-liquids (GTL) to increase the conversion and premium of the end product; it might not be necessary when the FB reactor is used paraffin synthesis.

For the separate production of Fischer-Tropsch fuels from synthesis, the synthesis gas is catalytically reacted over Fischer-Tropsch catalysts to produce hydrocarbon fuels in a slurry-phase reactor. The unconverted synthesis gas is then recycled to the synthesis unit to complete the conversion to fuels. The overall efficiency for this process on a higher heating value (HHV) basis is approximately 60%.

The liquid fuels consist of sulfur-free naphtha and high cetane diesel. By optimizing operating parameters, production of high-quality diesel fuel can be maximized. In these cases, the resulting fuel mix is one-third naphtha and two-thirds diesel fuel.

Although gas-to-liquids is an established technology, the biomass-to-liquids (BTL) process is a completely new approach, which requires the development of new technologies (biomass treatment, biomass gasification, hot gas clean up, new Fischer-Tropsch catalysts, advance wax upgrading) especially toward the reduction of the cost of the process. However, the big advantage of biomass-to-liquid fuels is that it is directly usable in the present day in transportation sector and furthermore, it may be suitable for future fuel cell vehicles via on board reforming since it is free of sulfur.

Biomass-to-liquids refineries can be located anywhere that carbonaceous feedstock is produced. This technology can produce clean transportation fuel using domestic coal thus expanding the supply of transportation fuels while decreasing dependence on overseas sources of energy.

See also: Fischer-Tropsch, Fischer-Tropsch Process, Fischer-Tropsch Catalysts, Fischer-Tropsch Chemistry, Fischer-Tropsch Commercial Processes, Synthesis Gas.

Fischer-Tropsch Process – Reactors

The most important aspects for development of commercial Fischer Tropsch (F-T) reactors are the high reaction heats and the large number of products with varying vapor pressures (gas, liquid, and solid hydrocarbon derivatives).

For large-scale commercial reactors, heat removal and temperature control are the most important design features to obtain optimum product selectivity and long catalyst lifetimes. Over the years, basically four Fischer-Tropsch reactor designs have been used commercially.

The fixed bed reactor consists of thousands of small tubes with the catalyst as surface-active agent in the tubes. Water surrounds the tubes and regulates the temperature by settling the pressure of evaporation. The slurry reactor is widely used and consists of fluid and solid elements, where the catalyst does not have a particular position but flows around as small pieces of catalyst together with the reaction components. Overheating the catalyst causes the decrease of activity and favors the deposition of carbon on the surface of particles.

The fixed bed reactor produces 13.3% C_4 , 18% gasoline (C_5 - C_{11}), 14% diesel (C_{12} - C_{18}), 7% C_{19} - C_{23} , 20% medium wax, and 25% hard wax. Originally fixed reactors, later in the form of multi tubular fixed bed (MTFB) reactors, were used. In the multi tubular form, these reactors are commercially used by Sasol in South Africa and by Shell in Malaysia. The reactor operates in the three-phase gas-liquid-solid trickle bed mode. A recent development is the slurry bubble column (SBC) reactor which is used commercially by Sasol.

In the slurry reactor, the catalyst is suspended in the liquid and the gas is bubbled through the suspension. Generally, this type of reactor gives (i) a more uniform temperature, (ii) there is less catalyst present and consumed per ton of product, and (iii) the differential pressure over bed is lower.

The slurry reactor and the fixed bed reactor are used in low temperature process. The fluidized bed reactors are diverse, but characterized by the fluid behavior of the catalyst; the fluidized bed reactor is used in the high-temperature Fischer-Tropsch process.

Sasol uses iron catalysts and operates several types of reactors, of which the slurry bubble column reactor is the most versatile (i.e., applied in the Sasol Slurry Phase Distillate; SSPD).

The Fischer-Tropsch synthesis in slurry bubble column reactors is attractive relative to fixed bed reactors. The advantages are: i) low pressure drop over the reactor, ii) excellent heat transfer characteristics resulting in stable reactor temperatures, iii) no diffusion limitations, iv) possibility of continuous refreshment of catalyst particles, and v) relatively simple construction and low investment costs. Sixty-three percent straight run liquid fuel can be obtained from a slurry bubble column reactor, with a selectivity of 89% conversion of (H_2 + CO) per pass. The product upgrading process provides considerable flexibility of product option that includes high-quality diesel and jet fuel, chemicals for manufacturing solvents, alcohol, polymers, and specialty such as lube oils and waxes.

The slurry bubble column reactor is simpler in construction than the multi tubular fixed bed reactor. The suspended cooling coils and a gas distributor give a cheaper arrangement than the tube and tube sheet arrangement in the multi tubular fixed bed reactor. Because of this, the slurry bubble reactor column may lend itself much better to scale up.

Fluidized bed reactors are ideally suited for production of lower molecular weight long chain hydrocarbon derivatives from synthesis gas. The fluidized bed (FB) reactor produces 43% C_4 -, 40% gasoline (C_5 - C_{11}), 7% diesel, and 4% medium wax. These reactors can operate only when all the reactants are in gaseous phase. The catalyst used is typically a fused and promoted Fe-catalyst, and the reactors operate at high temperatures (high reaction rates) in order to avoid formation of high molecular weight products, which would wet catalyst particles and have an adverse effect on their fluidization properties.

See also: Fischer-Tropsch, Fischer-Tropsch Process, Fischer-Tropsch Catalysts, Fischer-Tropsch Chemistry, Fischer-Tropsch Commercial Processes, Synthesis Gas.

Fixed-Bed Incinerator or Moving-Grate Incinerator

The fixed or moving grate incinerator is a large, fixed hearth incinerator with a moving grate. The moving grate enables the movement of waste through the combustion chamber to be optimized to allow a more efficient and

complete combustion. These incinerators are typically used for combustion of municipal waste, and are thus referred to as municipal solid waste incinerators (MSWIs).

In the fixed bed incinerator or moving grate incinerator, the waste is introduced by a crane through the throat at one end of the grate, from where it moves down over the descending grate to the ash pit in the other end. Here, the ash is removed through a water lock. Part of the combustion air (primary combustion air) is supplied through the grate from below. This air flow also has the purpose of cooling the grate itself. Cooling is important for the mechanical strength of the grate, and many moving grates are also water-cooled internally. Secondary combustion air is supplied into the boiler at high speed through nozzles over the grate. It facilitates complete combustion of the flue gases by introducing turbulence for better mixing and by ensuring a surplus of oxygen.

The incinerator must be designed to ensure that the flue gas reaches a temperature of at least 850°C (1,560°F) in order to ensure proper breakdown of organic toxins. This includes backup auxiliary burners (often fueled by oil), which are fired into the boiler in case the heating value of the waste becomes too low to reach this temperature alone. The flue gases are then cooled by heat transfer and heat the steam to typically 400°C at a pressure of 550 to 600 psi bar for the electricity generation in the turbine. At this point, the flue gas has a temperature of around 200°C, and is passed to the flue gas cleaning system.

See also: Combustion, Incinerators.

Fish Oil

Although long recognized as a source of nutrients, fish oil contains omega-3 fatty acids that can be absorbed easily. Fish oil contains both docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA). There is evidence from multiple studies supporting intake of recommended amounts of docosahexaenoic acid and eicosapentaenoic acid in the form of dietary fish or fish oil supplements which lowers triglycerides, reduces the risk of death, heart attack, dangerous abnormal heart rhythms, and strokes in people with known cardiovascular disease, slows the buildup of atherosclerotic plaques (hardening of the arteries), and lowers blood pressure slightly. Fish oil comes from cold water fish such as mackerel, tuna, salmon, cod, and many other fish.

Fish oil is also a potentially good source of fatty acids for the production of bio-oil. Waste fish oil can be converted into bio-oil by a fast pyrolysis process at 525°C (975°F) in a continuous pilot plant reactor with a yield on the order of 72% w/w. Many different chemical groups can be produced during the pyrolysis reaction, and the liquid product (bio-oil) obtained from triglyceride pyrolysis has a complex composition. This bio-oil can be used directly as fuel or can be fractionated to obtain purified hydrocarbon derivatives in the range of gasoline and diesel.

Fish oil is considered as one of the raw materials for the production of biodiesel as it contains more than 60 different fatty acids. Among which, nearly 80-85% of these are grouped into four category of fatty acids such as (i) C14:0 and C16:0, (ii) C16:1 and C18:1, (iii) C20:1 and C22:1, and (iv) C20:5, C22:5, and C22:6. Fish oil is enriched with eicosapentaenoic acid and docosahexaenoic acid, which represents more than 90% of all the polyunsaturated fatty acids. Thus, fish oil is potential feedstock for producing biodiesel.

See also: Black Liquor, Fatty Acids, Fish Oil, Tall Oil.

Fixed-Bed Process

A fixed-bed (as applied to a reactor) is a stationary bed (of catalyst in the reactor) that is used to accomplish a process.

Fixed bed reactors resemble multi-tube heat exchangers, with the catalyst packed in vertical tubes held in a tube-sheet at the top and the bottom of the tubes. Uniform packing of catalyst within the tubes is important to ensure uniform pressure drop, flow, and residence time through each tube. Reaction heat is removed by generating steam on the shell side of the reactor, or by flowing some other heat transfer fluid through it. However, temperature control is more difficult in a fixed bed than in a fluid bed reactor because localized hot spots can develop in the tubes. The tendency to develop hot spots can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in proportions that vary along the length of the tubes, so that there is low catalyst activity at the inlet, but the activity steadily increases to a maximum at the outlet. Another remedy is to pack the tubes with catalysts having

a progressively higher loading of cupric chloride so as to provide an activity gradient along the length of the tubes. Multiple reactors in series are also used in fixed bed oxy-chlorination, primarily to control heat release by staging the air or oxygen feed. Each successive reactor may also contain a catalyst with a progressively higher loading of cupric chloride. These methods of staging the air or oxygen feed and of grading the catalyst activity work to flatten the temperature profile and allow improved temperature control. Compared with the fluid bed process, fixed bed oxy-chlorination generally operates at a higher temperature (230 to 300°C, 445 to 570°F) and high gauge pressure.

See also: Fixed-Bed Reactor.

Fixed-Bed Reactor or Moving-Bed Reactor

In the fixed-bed reactor, the feedstock is supported by a grate and the gasifying media (steam, air, or oxygen) pass upward through the supported bed, whereby the product gases exit from the top of the reactor.

In the moving-bed reactor, the feedstock and gaseous streams move countercurrently, i.e., the carbonaceous feedstock moves downward by gravity and gas passes upward through the feedstock bed. The temperature at the bottom of the reactor is higher than that at the top. Because of the lower temperature at the top for feedstock devolatilization, relatively large amounts of liquid hydrocarbon derivatives are also produced in this type of gasifier.

In both types of the reactor, the residence time of the feedstock is much longer than that in a suspension reactor, thus providing ample contact time between reactants. Ash is removed from the bottom of the reactor as dry ash or slag – Lurgi and Wellman-Galusha gasifiers are examples of this type of reactors.

A moving bed reactor is classified as a kind of fixed-bed reactors since solids in the bed stay together as a bed regardless of the movement of the hardware that supports the bed.

See also: Gasification, Gasifiers.

Fixed Carbon

Fixed carbon is the combustible residue left after the volatile matter is driven off. It is, in fact, a measure of the solid combustible material in the carbonaceous feedstock after the expulsion of volatile matter and, like the determination of the carbon residue of crude oil and crude oil products, represents the approximate yield of thermal coke from the carbonaceous feedstock.

The fixed carbon value is one of the values used in determining the efficiency of the combustion equipment. It is a measure of the solid combustible material that remains after the volatile matter in the carbonaceous feedstock has been removed. For this reason, it is also used as an indication of the yield of coke in a coking process. Fixed carbon plus ash essentially represents the yield of coke.

The fixed carbon value is determined by subtracting from 100 the resultant summation of moisture, volatile matter, and ash with all percentages on the same moisture reference base (ASTM D3172). Fixed carbon values, corrected to a dry, mineral-matter-free basis, are used as parameters in the coal classification system (ASTM D388).

As an interesting comparison, the test for determining the carbon residue (Conradson), i.e., the coke-forming propensity of crude oil fractions and crude oil products (ASTM D189; ASTM D2416) advocates the use of more than one crucible. A porcelain crucible is used to contain the sample, and this is contained within two outer iron crucibles. This corresponds to the thermal decomposition of the sample in a limited supply of air (oxygen) and the measurement of the carbonaceous residue left at the termination of the test.

See also: Proximate Analysis.

Flammability

Flammability is the ease with which a substance will burn or ignite, causing fire or combustion. Flammable materials are materials (usually individual chemical or mixture of hydrocarbon derivatives) which have a low flash point and

ignite with little provocation. Hydrocarbon gases and liquid from any source are flammable insofar as they will burn readily in air. Any substance that can burn is considered flammable and/or combustible. The real threat of fire lies with flammable materials, which are substances that are more likely to burn and will ignite more rapidly.

The United States Department of Transportation (USDOT) is responsible for determining what constitutes a flammable material, and has offered the following definitions for ignitable materials:

Combustible Liquid

Any liquid having a flash point above 100°F and below 200°F

Flammable Liquid

Any liquid having a flash point below 100°F

Flammable Gas

A compressed gas that satisfies the criteria for flame projection, lower flammability limit, and flammability range

Flammable Solid

A non-explosive material that is capable of producing fire as a result of friction, heat retained from production or which, if ignited, produces a serious transportation hazard.

These definitions are based on the flammability characteristics of the material, specifically the *flash point* which is the minimum temperature at which a liquid gives off vapor in sufficient concentrations to allow the substance to ignite.

As an aid in identifying the chemicals which pose a flammability hazard in the laboratory, all chemical manufacturers are required to include relevant information on the chemical label. One of the most common grading systems is that developed by the National Fire Protection Association (NFPA). In this system, chemicals are rated from 0 (non-flammable) to 4 (extremely flammable) (Table F-5). It is important for all laboratory personnel to recognize and become familiar with the NFPA diamond and understand the grading levels established by the NFPA for flammable materials. The red portion of the diamond gives an indication of the flammability of the material.

Table F-5 The NFPA system for flammability rating.

Rating	Hazard Description
0	Materials that will not burn.
1	Materials that must be preheated before they will ignite.
2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before they will ignite.
3	Liquids and solids that can ignite under almost all temperature conditions.
4	Materials which will rapidly vaporize at atmospheric pressure and normal temperatures, or are readily dispersed in air and which burn readily.

Another warning that indicates that a material is flammable is the presence of the flame on the chemical label. This is a standard symbol required by the United States Department of Transportation to be used on all packages offered for transport over public highways, airways, or by sea, which carry materials classified as an ignition hazard.

The flashpoint provides information related to the flammability of a chemicals or a crude oil product (Table F-6). Many of the common organic solvents and chemicals used in the laboratory have flash points well below room temperature. At or above the flash point temperature, there exists sufficient vapor, in correct concentration, to ignite if an ignition source is provided. Though the flashpoint provides a baseline for danger, other conditions may exist which would lower the flashpoint below the accepted value.

Table F-6 US DOT classification of flammable materials.

Classification	Terminology	Flash Point/Boiling Point
1A	Flammable	FP: <73°F; BP <100°F
1B	Flammable	FP: <73°F; BP >100°F
1C	Flammable	FP: 73°F; BP <100°F
II	Combustible	FP: at or >100°F
IIIA	Combustible	FP/BP: at or >140°F
IIIB	Combustible	FP/BP: at or >200°F

In mixtures of hydrocarbon derivatives, it is well worth remembering that the flash point of the mixture corresponds to the flash point of the most flammable (usually the lowest boiling) component of the mixture. Many workers and professionals use an average flash point for a mixture – much to their own detriment and the danger to themselves and colleagues.

It is important to recognize what constitutes an ignition hazard. Many fires occur because people are unaware of what is a hazard, or are careless when working with flammables around potential ignition sources. Each flammable substance has a corresponding flammable range at which concentrations a fire may result if an ignition source is at hand. The flammability range consists of an upper and lower concentration boundary that indicates where the danger lies – be the 2 limits. The flammability range is very wide for some chemicals – for example, acetaldehyde (CH_3CHO), carbon disulfide (CS_2), ether, (diethyl ether, $\text{C}_2\text{H}_5)_2\text{O}$), and methanol (CH_3OH). Such chemicals are particularly hazardous because the window for ignition is much wider – increased caution must be exercised when using these materials.

Flammability Range

The flammability range is expressed by the lower explosive limit (LEL) and the upper explosive limit (UEL). The lower explosive limit is the concentration of natural gas in the air below which the propagation of a flame will not occur on contact with an ignition source. The lower explosive limit for natural gas is 5% by volume in air, and, in most cases, the smell of gas would be detected well before combustion conditions are met. The upper explosive limit is the concentration of natural gas in the air above which the propagation of a flame will not occur on contact with an ignition source. The natural gas upper explosive limit is 15% by volume in air.

Flash Point

The flash point is the temperature to which gas must be heated under specified conditions to give off sufficient vapor to form a mixture with air that can be ignited momentarily by a specified flame (ASTM D56, ASTM D92, ASTM D93) – dependent on the composition of the gas and the presence of other hydrocarbon constituents.

Thus, the flash point is that minimum temperature at which there is a sufficient concentration of evaporated fuel in the air for combustion to propagate after an ignition source has been introduced. At this temperature, the vapor may cease to burn when the source of ignition is removed.

A slightly higher temperature, the fire point, is defined as the temperature at which the vapor continues to burn after being ignited, even when the source of ignition is removed. Neither of these parameters is related to the temperatures of the ignition source or of the burning liquid, which are much higher. The flash point is often used as one descriptive characteristic of liquid fuel, but it is also used to describe liquids that are not used intentionally as fuels.

Every flammable liquid has a vapor pressure, which is a function of temperature. As the temperature increases, the vapor pressure increases. As the vapor pressure increases, the concentration of evaporated flammable liquid in

the air increases. Hence, temperature determines the concentration of evaporated flammable liquid in the air under equilibrium conditions.

There are two basic standard (ASTM) test methods for measurement of the flash point measurement: (i) the open cup methods and (ii) the closed cup methods which produce the desired data.

In the open cup method, the sample is contained in an open cup which is heated, and at intervals, a flame is brought over the surface. The measured flash point will actually vary with the height of the flame above the liquid surface, and at sufficient height, the measured flash point temperature will coincide with the fire point. Examples include Cleveland Open Cup and Pensky-Martens open cup. The main difference is that the former is heated from below, while the latter is heated from the sides as well as from below.

However, the flash point is an empirical measurement rather than a fundamental physical parameter. The measured value will vary with equipment and test protocol variations, including temperature ramp rate (in automated testers), time allowed for the sample to equilibrate, sample volume, and whether the sample is stirred.

As with other properties, the flash point of a mixture, such as a gas stream or a low-boiling liquid mixture, is the flash point of the most volatile constituent in the mixture and, thus, is dependent on the composition of the gas stream and the presence of other constituents of the liquid mixture. The flash point is also used to detect contamination. A substantially lower flash point than expected for a product is a reliable indicator that a product has become contaminated with a more volatile product. The flash point is also an aid in establishing the identity of a particular product.

A slightly higher temperature, the fire point, is defined as the temperature at which the vapor continues to burn after being ignited, even when the source of ignition is removed. Neither of these parameters is related to the temperatures of the ignition source or of the burning liquid, which are much higher. The flash point is often used as one descriptive characteristic of liquid fuel, but it is also used to describe liquids that are not used intentionally as fuels.

See also: Fire Point and Flash Point, Flammability, Flammability Range.

Flash Pyrolysis

Pyrolysis is the thermal decomposition of organic substances by heating in the absence of air or an oxidizing agent, or with such a limited supply that gasification does not occur to an appreciable extent or may be described as partial gasification. A relatively low temperature is employed of 500 to 800°C (930 to 1,470°F), compared to 800 to 1,000°C (1,470 to 1,830°F) for gasification. Three products are usually produced: gas, pyrolysis oil, and a carbon-rich residue (char), the relative proportions of which depend very much on the pyrolysis method, the characteristics of the shale (kerogen) biomass, and the reaction parameters.

The premise is that when a carbonaceous material is heated very rapidly to temperatures in excess of those required for decomposition, fragmentation of the carbonaceous feedstock is very extensive thereby releasing the liquids from the carbonaceous feedstock matrix (and reducing the residence time of the liquids within the (solid) feedstock before secondary reactions to gaseous products can occur. This is especially true in view of the enhanced yields of volatile (liquid and gaseous) products that can be obtained, relative to the standard pyrolytic methods of the carbonaceous feedstock decomposition treatment as well as the standard thermal methods of the carbonaceous feedstock analysis (such as ASTM D3175).

Some of the techniques that are applicable to the flash pyrolysis are (i) laser, (ii) microwave, (iii) flash tube, (iv) plasma, (v) electric arc, (vi) shock tube, (vii) electric current, and (viii) entraining gas.

Lasers have been employed to produce extremely high temperatures as has microwave heating of carbonaceous feedstocks. Both techniques produce considerable quantities of acetylene, and the extent of the carbonaceous feedstock conversion depends on the volatile matter content of the carbonaceous feedstock, suggesting that the fixed carbon of the carbonaceous feedstock is not a predominant factor.

Flash tubes with short (microsecond or millisecond) irradiation times also produce acetylene as one of the major products, and there appears to be little tar production. The presence of hydrogen reduces the amount of acetylene produced.

Plasmas, which are often produced by exposing a gas stream to an electric arc, are capable of generating temperatures in excess of 10,000°C (>18,000°F). The extent of the reaction depends on the volatile matter content of the carbonaceous feedstock as well as on the particle size, and acetylene is the principal product – the yield of acetylene is increased by the presence of hydrogen.

Electric arc pyrolysis as a means of the carbonaceous feedstock decomposition is accomplished by passing a high-intensity electric arc between two electrodes, one of which is made of the carbonaceous feedstock. The products are mainly methane, acetylene, and ethylene with a notable absence of liquid products.

Shock tubes produce transient regions of high temperature and high pressure. The products from shock tube pyrolysis have been higher in the proportion of unsaturated hydrocarbon derivatives, but the overall conversion is low.

Techniques using an electric current as the source of heat usually attain lower temperatures than the previous methods, and the yields of acetylene are much lower. However, this technique has shown that (i) substantial yields of volatile matter can be achieved at high heating rates, (ii) hydrogen is the principal product of the carbonaceous feedstock decomposition at high temperatures, and (iii) the yields from hydrolysis of the carbonaceous feedstock are increased if the particle size of the carbonaceous feedstock is decreased.

The method using an entraining gas is amenable to commercial ventures. High conversion of the carbonaceous feedstock at 900°C (1,650°F) to volatile products (predominantly methane along with other hydrocarbon gases) has been reported. Although water is normally excluded along with other reagents during pyrolysis, the term hydrolysis has also been applied to the decomposition of organic material in the presence of superheated water or steam (hydrous pyrolysis).

The Karrick process is a low-temperature carbonization and pyrolysis process of carbonaceous materials. Although primarily meant for coal carbonization, it also could be used for processing of other carbonaceous materials. In the process, the feedstock is heated at 450 to 700°C (800 to 1,300°F) in the absence of air to distill out synthetic liquid fuel and gas.

Flash Vaporization

Condensate stabilization by flash vaporization is a relatively simple operation employing only two or three flash tanks. This process is similar to stage separation utilizing the equilibrium principles between vapor and condensate phases. Equilibrium vaporization occurs when the vapor and condensate phases are in equilibrium at the temperature and pressure of separation.

Condensate from the inlet separator after passing through the exchanger enters to the high-pressure flash tank, where the pressure is maintained at 600 psia. A pressure drop of 300 psia is obtained here, which assists flashing of large amounts of lower-boiling constituents, which join the sour vapor stream after recompression. The vapor can either be processed further and put into the sales gas or be recycled into the reservoir and used as gas lift to produce more crude oils. The bottom liquid from the high-pressure tank flows to the middle-pressure flash tank operated at 300 psia. Additional methane and ethane are released in this tank. The bottom product is withdrawn again to the low-pressure tank operated at 65 psia. To ensure efficient separation, condensate is degassed in the stripper vessel at the lowest possible pressure prior to storage. This reduces excess flashing of condensate in the storage tank and reduces the inert gas blanket pressure required in it.

Note that flash vaporization as a condensate stabilization method is old technology and is not often used in a modern gas cleaning plant. However, variations of flash technology might also be found on oil production facilities stabilizing liquid organic products.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Flax and Flaxseed Oil

Flaxseed is one of the richest plant sources of the ω -3 fatty acid, i.e., α -linolenic acid (ALA) and lignans (phytoestrogens). Flaxseeds are available in two basic varieties, which are (i) brown, and (ii) yellow or golden. Both have similar

characteristics and equal numbers of short-chain ω -3 fatty acids. The exception is a type of yellow flax called solin (trade name Linola), which has a completely different oil profile and has a low ω -3 fatty acid content. Brown flax is better known as an ingredient in paints, varnish, fiber, and cattle feed. Flaxseed is a multicomponent system with bio-active plant substances such as oil, protein, dietary fiber, soluble polysaccharides, lignans, phenolic compounds, vitamins (A, C, F, and E), and minerals (P, Mg, K, Na, Fe, Cu, Mn and Zn).

Flaxseed is the richest plant source of the ω -3 fatty acid, i.e., α -linolenic acid (ALA) but is low in saturated fatty acids, moderate in monosaturated fatty acids (18 %), and rich in polyunsaturated fatty acid. Of all lipids in flaxseed oil, α -linolenic acid is the major fatty acid followed by oleic, linoleic, palmitic, and stearic acids. Although flaxseed oil is naturally high in anti-oxidant like tocopherols and beta-carotene, traditional flaxseed oil gets easily oxidized after being extracted and purified.

The major insoluble fiber fraction consists of cellulose and lignin, and the soluble fiber fractions are the mucilage gums. The mucilage can be extracted by water and has good foam-stabilizing properties. Mucilage gums are polysaccharides that become viscous when mixed with water or other fluids.

Plant lignans are phenolic compounds formed by the union of two cinnamic acid residues. Lignans are ubiquitous within the plant kingdom and are present in almost all plants. Besides lignans, other phenolic compounds found in flaxseed are p-coumaric acid and ferulic acid.

Surplus biomass from the production of flax shives, and generated from *Brassica carinata*, a yellow-flowered plant related to those which engulf fields in spring, can be used to produce bioethanol. The shives, also known as shoves or boon, are the wooden refuse removed during processing flax, hemp, or jute, as opposed to the fibers (tow).

See also: Linseed Oil.

Flexible-Fuel Vehicle

A flexible fuel (or flex fuel) is an alternative fuel made of a combination (blend) of gasoline and methanol or ethanol. Thus, a flexible-fuel vehicle (flex-fuel vehicle or sometimes referred to as a dual-fuel vehicle) is a vehicle that can run alternately on two or more sources of fuel; it includes cars capable of running on gasoline and gasoline/ethanol mixtures, as well as cars that can run on both gasoline and methane-rich gas streams. Flexible fuel vehicles (FFVs) have an internal combustion engine and are capable of operating on gasoline and any blend of gasoline and ethanol up to 83%. E85 (or flex fuel) is a gasoline-ethanol blend containing 51% to 83% v/v ethanol, depending on geography and season.

Other than an ethanol-compatible fuel system and a different powertrain calibration, Flexible fuel vehicles are similar to their conventional gasoline-only counterparts. While fuel economy (miles per gallon) is generally lower with increased levels of ethanol (due to the lower energy content in ethanol as compared to gasoline and because the engines are optimized for gasoline), many flexible-fuel vehicles have improved acceleration performance when operating on higher ethanol blends.

Flexible-fuel engines are capable of burning any proportion of the resulting blend in the combustion chamber as fuel injection and spark timing are adjusted automatically according to the actual blend detected by electronic sensors. Flexible-fuel vehicles are distinguished from bi-fuel vehicles, where two fuels are stored in separate tanks and the engine runs on one fuel at a time, for example, compressed natural gas (CNG), liquefied petroleum gas (LPG), or hydrogen.

Typically, flexible fuel vehicles are designed to run on gasoline or a blend of up to 85% ethanol (E85). Except for a few engine and fuel system modifications, they are identical to gasoline-only models. Flexible fuel vehicles experience no loss in performance when operating on E85.

See also: Blended Fuels, Blending, Ethanol, Methanol.

Flexsorb Process

The Flexsorb process is a process that uses sterically hindered amines (olamines) in aqueous solutions or other physical solvents; the molecular structure hinders the carbon dioxide approach to the amine and preferentially removes hydrogen sulfide from the gas stream.

The sterically hindered amines are secondary amines that have a large hydrocarbon group attached to the nitrogen group. The large molecular structure hinders the carbon dioxide approach to the amine. The larger the structure, the more difficult it becomes for the carbon dioxide to get close to the amine. They also appear to be unstable to the carbamate form of product and revert easily to the carbonate form found in the tertiary amines. Like tertiary amines, they are capable of a high degree of solvent loading – 1 mole/mole, instead of 0.5 mole/mole typical of primary and secondary amines.

The Flexsorb SE process is based on a family of sterically hindered amines in aqueous solutions or other physical solvents. The sterically hindered amines are secondary amines that have a large hydrocarbon group attached to the nitrogen group. The large molecular structure hinders the carbon dioxide approach to the amine. The larger the structure, the more difficult it becomes for the carbon dioxide to get close to the amine. They also appear to be unstable to the carbamate form of product and revert easily to the carbonate form found in the tertiary amines. Like tertiary amines, they are capable of a high degree of solvent loading—1 mole/mole, instead of 0.5 mole/mole typical of primary and secondary amines. One version of the solvent, Flexsorb SE Plus, is very selective toward hydrogen sulfide and has been used in several plants for tail gas processing or lean acid gas enrichment (AGE).

There are two mixed hindered amine/physical solvent versions of the Flexsorb process. The Hybrid Flexsorb SE process employs a solution of the Flexsorb SE amine, water, and an unspecified physical solvent. The Flexsorb PS solvent consists of a different hindered amine, water, and a physical solvent.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Flocculation

Flocculation is the further enlargement of agglomerated particles by either the presence of sticky metal hydroxides or the addition of an organic polymer. The suspension is gently mixed to allow bridges to form between particles which binds the particles together into larger agglomerates (flocs). The formation of these larger flocs is enhanced by mild mixing, while intense mixing breaks the bridges and redisperses the particles. Some additives such as aluminum sulfate (alum), ferric salts, and certain ionic polymers (polyelectrolytes) can enhance both agglomeration and flocculation.

The aluminum and iron salts hydrolyze to form insoluble aluminum or iron hydroxide gels, which form flocs that collect and trap colloidal materials. The polyelectrolytes are polymers of water-soluble organic molecules which are large organic molecules having polar groups spaced along their length. These polar groups can be cationic, anionic, or non-ionic. The ionic groups give the polymer water solubility as well as the ability to dissociate and form a polymer molecule with ionic charges spaced along its length.

The polymers work by dissociation of the ionic sites in the polymer, thus providing ionic charges on the polymer. The ionic charges then interact with the charge on the colloidal particles and form flocs by collecting a lot of individual particles to a single polymer molecule. They also bridge from one polymer molecule to another. Cationic polymers contain nitrogen in amine or quaternary ammonium groups as the active sites. Anionic polymers contain carboxylic, sulfate, sulfonate, phosphate, or any of the ionizable derivatives of mercaptan groups. The non-ionic polymers work by attracting the charges on the particles to the polar sites in the polymer, which normally contain oxygen as alcohol, ether, aldehyde, or ketone groups.

See also: Chemical Precipitation, Coagulation, Sedimentation.

Flue Gas

Flue gas (sometimes called *exhaust gas* or *stack gas*) is the gas that emanates from combustion plants and which contains the reaction products of fuel and combustion air and residual substances such as particulate matter (dust), sulfur oxides, nitrogen oxides, and carbon monoxide. When burning coal and/or waste materials, hydrogen chloride and hydrogen fluoride may be present in the flue gas as well as hydrocarbon derivatives and heavy metal derivatives. In many countries, as part of a national environmental protection program, exhaust gases must comply with strict governmental regulations regarding the limit values of pollutants such as dust, sulfur and nitrogen oxides, and

carbon monoxide. To meet these limit values, combustion plants are equipped with flue gas cleaning systems such as gas scrubbers and dust filters.

As with other gases, the composition of flue gas depends on the type of fuel and the combustion conditions, e.g., the air ratio value. Many flue gas components are air pollutants and must therefore, due to governmental regulations, be eliminated or minimized by special cleaning procedures before the gas is released to the atmosphere. For example, flue gas produced by the combustion of fossil fuels, such as coal and crude oil, can contain a significant amounts of sulfur derivatives. In fact, when carbonaceous fuels, such as fossil fuels, are burned, approximately 90%+ w/w of the sulfur in the feedstock is converted to sulfur dioxide (SO_2), which occurs under normal conditions of temperature in the furnace and the oxygen fed to the combustor. However, when there is an excess of oxygen present, the sulfur dioxide is oxidized to sulfur trioxide (SO_3), and at higher temperatures (approximately 800°C, 1470°F), the formation of sulfur trioxide is favored.

As with other gases, the composition of flue gas depends upon the composition and properties of the fuel being combusted but, nevertheless, the composition will usually consist predominantly of nitrogen (usually on the order of 60% v/v and higher derived from the combustion process using air as the oxidant, carbon dioxide, and water vapor), as well as any excess oxygen (also derived from the air). Flue gas can also contain a small percentage of a number of pollutants, such as (i) particulate matter, for example soot, (ii) carbon monoxide, (iii) nitrogen oxides, NO_x , and (iv) sulfur oxides, SO_x . The potential for the presence of hydrocarbon derivatives is low unless the combustion process used a minimal of air and then also uses a hydrocarbonaceous feedstock. The particulate matter is composed of small particles of solid materials and small liquid droplets which give flue gases their smoky appearance. The nitrogen oxides are derived from the nitrogen in the ambient air as well as from any nitrogen-containing compounds in the fuel. The sulfur dioxide is derived from any sulfur-containing compounds in the fuel.

At power plants, flue gas is often treated with a series of chemical processes and scrubbers, which remove pollutants such as sulfur dioxide and sulfur trioxide. Flue gas desulfurization units capture the sulfur dioxide (and the sulfur trioxide, if present), and electrostatic precipitators or fabric filters remove particulate matter produced by burning fossil fuels, particularly coal. Nitrogen oxides are treated, either by modifications to the combustion process to prevent their formation, or by high temperature or catalytic reaction with ammonia (NH_3) or urea (H_2NCONH_2). In either case, the aim is to produce nitrogen gas, rather than nitrogen oxides. In the United States, there is a rapid deployment of technologies to remove mercury from flue gas (Scala et al., 2013). This is typically accomplished by absorption on sorbents or by capture in inert solids as part of the flue gas desulfurization process. Such scrubbing can lead to meaningful recovery of sulfur for further industrial use.

Examples of common flue gas cleaning processes are: (i) a wet scrubbing process, which uses a slurry of alkaline sorbent, usually limestone or lime, or seawater to scrub the gases, (ii) a spray-dry scrubbing process, which uses similar sorbent slurries as described in the first category, (iii) a wet sulfuric acid process, which allows the recovery of sulfur in the form of commercial-quality sulfuric acid, (iv) a process commonly referred to as a SNOX flue gas desulfurization process, which removes sulfur dioxide, nitrogen oxides, and particulate matter from flue gases, and (v) a dry sorbent injection process, which introduces powdered hydrated lime or other sorbent material into the exhaust ducts to eliminate sulfur dioxide and sulfur trioxide from the process emissions.

In terms of flue gas (and biogas) cleaning, the separation of the acid gaseous pollutants, the separation of hydrogen chloride, sulfur dioxide, and hydrogen fluorides (and any vestiges thereof), is essential. These gases form the greater part of the polluting constituents effected by absorption, preferentially by means of lime products [CaO , $\text{Ca}(\text{OH})_2$] and also by sodium-based products (NaOH , NaHCO_3 , and Na_2CO_3). The available gas cleaning processes for the absorption of the acid gaseous pollutants can be classified into the following three groups: (i) dry sorption, spray absorption/drying, and (iii) wet scrubbing.

The separation of the fly ash and the metals occurring in the form of particulate matter at the boiler outlet takes place likewise via filtration, so that this process step can be integrated into the absorption process for the acid gaseous pollutants. The separation of dioxins, furans, and those metals, in particular mercury, present in gaseous form at the boiler outlet generally takes place by adsorption on activated carbon, zeolites, open hearth furnace coke, or bentonite. For adsorption, either static or a moving bed adsorber unit or a filter layer adsorber unit may be employed which offers the possibility of integration of the adsorption process with the filtering out of fly ash and reaction products from the four basic gas cleaning concepts. Removal of nitrogen oxides (NO_x) from the flue gases can be achieved in conjunction with the above pollution control systems by the use of selective non-catalytic reduction (SNCR).

Flue gas composition depends upon the composition and combustion-related characteristics of fuels and the degree of completion of combustion. This is the function of design of combustion equipment - burner, furnace, and application.

Fuels from crude oil can be divided into two classes which are (i) natural gas and (ii) manufactured gas, their main source of heat being carbon and hydrogen. The manufactured crude oil fuels are designated according to their boiling range and applications. However, they are generally known by their commercial names like LPG, petrol/gasoline/gas, kerosene/luminosity oil, diesel/high speed diesel/light diesel, fuel oil/furnace oil, and bunker oil. The hydrogen and carbon contents of a particular boiling cut remain more or less the same everywhere; however, impurities like vanadium, magnesium, and iron vary from one source of crude to another. In general, CO_2 , SO_2 , N_2 , O_2 and steam/water vapors are the main constituents of flue gases. CO , SO_3 , oxides of vanadium, magnesium, and iron shall also appear in certain applications. In practice, two values of flue gas composition – theoretical and measured – are used for designing and planning of pollution control measures.

Two types of combustion processes are generally deployed – continuous and cyclic. In a continuous process, fuel is admitted through a burner to produce continuous flame and gases which heat the product by directly coming into contact with the charge. In the indirect method, heat from flue gas flows to the charge through the container. The cyclic combustion, a fixed quantity of fuel in the form of vaporized or atomized liquid droplets, is admitted into combustion space, burnt, and then the products of combustion after providing thrust to a piston leaves through a pipe and a silencer. This cycle is repeated with a fresh quantity of fuel. Each cycle takes a fraction of a second to complete. In case of cyclic combustion, time and combustion space are more important parameters.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Flue Gas Cleaning

The quantity of pollutants in the flue gas from incineration plants is reduced by several processes.

Particulate matter is collected by particle filtration, most often electrostatic precipitators and/or baghouse filters. Hydrogen chloride and sulfur dioxide are removed in scrubbers or as dry desulfurization by injection of limestone slurry into the flue gas before the particle filtration. Wastewater from scrubbers must subsequently pass through a wastewater treatment plant. Nitrogen oxide emissions are either reduced by catalytic reduction with ammonia in a catalytic converter or by a high temperature reaction with ammonia in the furnace. Heavy metals are often adsorbed on injected activated carbon, which is collected by the particle filtration.

Incineration produces fly ash and bottom ash just as is the case when coal is combusted. The total amount of ash produced by municipal solid waste incineration ranges from 15 to 20% by weight of the waste and the fly ash amounts to 0 to 10% of the total ash. The fly ash, by far, constitutes more of a potential health hazard than does the bottom ash because the fly ash often contains high concentrations of heavy metals such as lead, cadmium, copper, and zinc as well as small amounts of dioxins and furans. The bottom ash seldom contains significant levels of heavy metals.

While fly ash is always regarded as hazardous waste, bottom ash is generally considered safe for regular landfill after a certain level of testing defined by the local legislation. Ash, which is considered hazardous, may generally only be disposed of in landfills which are carefully designed to prevent pollutants in the ash from leaching into underground aquifers – or after chemical treatment to reduce its leaching characteristics.

In spite of the promise shown by the use of incinerators for waste disposal and, in some cases, energy production (in the form of fuel gases), the use of incinerators for waste management is controversial.

See also: Bottom Ash, Fly Ash, Gas Cleaning, Gas Processing, Gas Treating. Incinerators.

Flue Gas Desulfurization

Flue gas desulfurization (FGD or scrubbing) is the removal of sulfur oxides from stack gases of a coal-fired boiler which uses coal to produce steam for the steam turbines that drive their electricity generators.

A primary feature of flue gas desulfurization is that it offers relatively low marginal cost for the removal of sulfur dioxide, especially when at least 90% removal is desired for an extended period.

Sulfur dioxide is responsible for acid rain formation and, as a result of environmental protection regulations regarding sulfur dioxide emissions, sulfur dioxide is now being removed from flue gases by a variety of methods, of which the most common are (i) wet scrubbing using a slurry of sorbents such as limestone (CaCO_3) or lime (CaO) to scrub the gases, (ii) spray-dry scrubbing using similar sorbent slurries such as limestone (CaCO_3) or lime (CaO), (iii) wet sulfuric acid process recovering sulfur in the form of commercial quality sulfuric acid, and (iv) dry sorbent injection systems.

Most flue gas desulfurization systems employ two stages for: (i) the removal of fly ash and (ii) the removal of sulfur dioxide. In wet scrubbing systems, the flue gas normally passes first through a fly ash removal device, either an electrostatic precipitator or a wet scrubber, and then into the sulfur dioxide absorber. In dry injection or spray drying operations, the sulfur dioxide is first reacted with the sorbent and then the flue gas passes through a particulate control device.

In wet flue gas desulfurization systems, the flue gas exiting the absorber is saturated with water and still contains some sulfur dioxide, raising the possibility of corrosion of downstream equipment. Two methods that minimize corrosion are: (i) reheating the gases to above their dew point and (ii) choosing construction materials and design conditions that allow equipment to withstand the corrosive conditions.

Advanced flue-gas desulfurization processes remove acid gas from burning coal without expensive scrubbers. Emissions from burning coal are piped into an absorber, where the acid gases react with an absorbing solution (such as a mixture of lime, water, and oxygen).

In the process, the gas is usually passed through particulate removal equipment (such as an electrostatic precipitator) after which the flue gas is increased in pressure and then cooled from approximately 130°C (265°F) to 80°C (175°F). It enters the lowest part of the absorber and is further cooled by water used to wash the inlet duct to prevent a buildup of solids.

The main sulfur dioxide absorption process occurs as the gas is scrubbed by a recirculating limestone slurry. This is taken from the bottom of the absorber and is sprayed downwards from nozzles arranged at five separate levels in the absorber tower. As a result of the process chemistry, the recirculating slurry becomes predominantly gypsum (CaSO_4) and a portion is continuously pumped away for gypsum separation and the removal of water using a hydrocyclone system. A wastewater treatment plant ensures any water from the flue gas desulfurization process returned to the environment meets quality standards set by the regulatory authority.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Fluid Bed

The fluid-bed (fluidized bed) of catalyst or coke is a bed that is agitated by an upward passing gas in such a manner that the particles of the bed simulate the movement of a fluid and has the characteristics associated with a true liquid.

A fluidized bed is formed when a quantity of a solid particulate substance (usually present in a holding vessel) is placed under appropriate conditions to cause the solid/fluid mixture to behave as a fluid (fluidization of the solid). This is usually achieved by the introduction of pressurized fluid through the particulate medium. This results in the medium then having many properties and characteristics of normal fluids, such as the ability to free-flow under gravity, or to be pumped using fluid-type technologies.

A fluidized bed consists of a fluid-solid mixture that exhibits fluid-like properties. As such, the upper surface of the bed is relatively horizontal, which is analogous to hydrostatic behavior. The bed can be considered to be an inhomogeneous mixture of fluid and solid that can be represented by a single bulk density.

Furthermore, an object with a higher density than the bed will sink, whereas an object with a lower density than the bed will float, thus the bed can be considered to exhibit fluid behavior. The density (the solid volume fraction of the suspension) of the bed can be altered by changing the fluid fraction, and objects with different density comparative to the bed can be caused to sink or float by altering either the fluid or solid fraction.

In fluidized beds, the contact of the solid particles with the fluidization medium (a gas or a liquid) is greatly enhanced when compared to packed beds. This behavior in fluidized beds enables good thermal transport inside the system and good heat transfer between the bed and its container. Similarly to the good heat transfer, which enables thermal uniformity analogous to that of a well-mixed gas, the bed can have a significant heat-capacity while maintaining a homogeneous temperature field.

Fluidized beds are used as a technical process which has the ability to promote high levels of contact between gases and solids. In a fluidized bed, a characteristic set of basic properties can be utilized, indispensable to modern process and chemical engineering; these properties include: (i) a high surface area contact between fluid and solid per unit bed volume, (ii) a high relative velocity between the fluid and the dispersed solid phase, (iii) high levels of intermixing of the particulate phase, and (iv) frequent particle-particle and particle-wall collisions.

Fluid-Bed Boiler

A fluid-bed boiler (fluidized bed boiler) is a large, refractory-lined vessel with an air distribution member or plate in the bottom, a hot gas outlet in or near the top, and some provisions for introducing fuel; the fluidized bed is formed by blowing air up through a layer of inert particles (such as sand or limestone) at a rate that causes the particles to go into suspension and continuous motion.

Fluidized bed boiler systems convert biomass and other solid or liquid fuels into steam energy. A fluidized bed thermal oxidizer is combined with advanced heat transfer technologies to cleanly and efficiently generate steam energy.

In addition to biomass, the system can be designed to accommodate tire-derived fuel (TDF) and refuse-derived fuel (RDF) containing wires. Fuel ash characteristics and upset operating conditions inevitably lead to occasional clinkering of a portion of the bed media. If a clinker is allowed to accumulate, this material would eventually destroy the fluidizing properties of the bed by increasing the average particle size of the bed material to a point where fluidization could no longer occur.

Fluid-Bed Catalytic Cracking

The fluid catalytic cracking (FCC, fluid bed catalytic cracking) process is the most widely used process and is characterized by the use of a finely powdered catalyst that is moved through the reactor, and flow patterns may vary depending upon the precise configuration of the reactor. The catalyst particles are of such a size that when *aerated* with air or hydrocarbon vapor; the catalyst behaves like a liquid and can be moved through pipes. Thus, vaporized feedstock and fluidized catalyst flow together into a reaction chamber where the catalyst, still dispersed in the hydrocarbon vapors, forms beds in the reaction chamber and the cracking reactions take place. The cracked vapors pass through cyclones located in the top of the reaction chamber, and the catalyst powder is thrown out of the vapors by centrifugal force. The cracked vapors then enter the bubble towers where fractionation into cracked low-boiling and high-boiling gas oils, cracked gasoline, and cracked gases takes place.

Since the catalyst in the reactor becomes contaminated with coke, the catalyst is continuously withdrawn from the bottom of the reactor and lifted by means of a stream of air into a regenerator where the coke is removed by controlled burning. The regenerated catalyst then flows to the fresh feed line, where the heat in the catalyst is sufficient to vaporize the fresh feed before it reaches the reactor, where the temperature is approximately 510°C (950°F).

Fluid catalytic cracking is the workhorse of the modern refinery worldwide. It is used to convert a high-boiling viscous crude oil feedstock such as vacuum gas oil (VGO), atmospheric residue (AR), vacuum residue (VR), and deasphalted oil (DAO), into lower-boiling and more usable products such as low-boiling olefin derivatives, naphtha, and kerosene. Since its first commercialization over a half of century ago, the fluid catalytic cracking process is still an evolving technology. Improvements in the technology as well as changing feedstocks and product requirements continue to drive this evolution.

The fluid catalytic cracking process consists of two key units: a reactor and a regenerator. The preheated oil and steam are mixed and introduced to the bottom section of the riser using feed nozzles. At the feed injection zone of the riser, oil is mixed with a stream of hot regenerated catalyst flowing down the inclined standpipe from the regenerator. The oil is heated further by the hot catalyst and vaporized. It is at this point at which the cracking reactions

occur. The hydrocarbon vapors formed initially by vaporization and successively by cracking carry the catalyst up the riser at 10 to 20 m/s by dilute phase pneumatic transport. At the exit of the riser, the spent catalyst and hydrocarbon derivatives are quickly separated using cyclone devices. The spent catalyst, which is partially deactivated by coke deposition in the riser, and the vapor, enter a disengager. The vapor stream is routed to a cyclone where entrained catalyst and catalyst fines are separated, and the vapor is removed from the cyclone overhead. The hydrocarbon vapors are fractionated into various product streams: cracking gas, gasoline, diesel, cycle oil, and slurry oil. The cycle oil is sent back to the riser for further cracking. In some cases, part of the slurry oil is also routed to the riser.

The spent catalyst flows down into the stripper where entrained hydrocarbon derivatives are steam stripped and removed. The spent catalyst flows through the inclined stripper standpipe into a fluidized bed regenerator. In the regenerator, air is introduced and distributed throughout the bed. The coke deposited on the spent catalyst is burned off. The regenerated catalyst is then routed to the bottom of the riser via the regenerator standpipe, where it is mixed with the feed oil and the riser operation continues. The regenerator flue gas leaving the fluidized catalyst bed contains entrained catalyst particles. Before leaving the regenerator, the flue gas is routed to the cyclone system where most of the entrained catalyst is recovered and returned to the catalyst bed. All the modern fluid catalytic cracking units are equipped with the following features: (i) a pre-lifting zone, (ii) feed nozzles, (iii) short residence, (iv) a cyclone system, (v) reaction terminating technology, sometimes referred to as quench technology, and (vi) oxidation catalysts.

A pre-lifting zone is a special device at the bottom of the riser to enhance the contact of catalyst and hydrocarbon feedstock. Also, feed nozzles are important to achieve a well-dispersed feed oil into the riser reactor, especially for heavier feedstocks. A new-generation feed nozzle has been developed by incorporating the principle of vaporization to produce fine droplets of high-boiling oil at a narrow droplet size distribution; with a Sauter mean diameter (SMD; i.e. average particle size) of 50 to 70 μm .

A short residence time (on the order of 2 to 3 seconds) while cracking reactions occur in a riser at 500 to 530°C (930 to 985°F). In addition, the installation of a high efficiency cyclone system at the riser exit facilitates quick separation of catalyst and hydrocarbon vapors. This is to prevent undesirable cracking after the catalyst and hydrocarbon mixture exit the riser.

The reaction terminating technology (quenching technology) is used to minimize undesirable secondary cracking reactions by quenching the riser reactor. Quenching media such as gasoline, diesel, or water are injected into a pre-determined location at the middle section of the riser and/or at the riser exit. The latter is commonly referred to as post-riser quenching. Also, special oxidation catalysts are used in the regenerator at 680 to 720°C (1,255 to 1,330°F), which convert carbon monoxide in the flue gas to carbon dioxide.

The key process variables for the FCC reactions are feedstock properties, reaction temperature and residence time, regenerator temperature, and catalyst-to-oil ratio. However, for an existing FCC unit, the variability of regeneration temperature and catalyst-to-oil ratio is limited due to hardware considerations.

See also: Quench.

Fluid-Bed Catalytic Cracking Unit

The fluidized-bed catalytic cracking unit (FCCU) is by far the most common catalytic cracking unit. In the fluidized-bed process, oil and oil vapor pre-heated to 260 to 425°C (500 to 800°F) is contacted with hot catalyst at approximately 705°C (1,300°F), either in the reactor itself or in the feed line (riser) to the reactor. The catalyst is in a fine, granular form which, when mixed with the vapor, has many of the properties of a fluid. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in the reactor, and any oil remaining on the catalyst is removed by steam stripping. The cracked oil vapors are then fed to a fractionation tower where the various desired fractions are separated and collected. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration by burning off the coke deposits with air.

Fluid-Bed Combustion

Fluid-bed combustion (fluidized bed combustion) is a process used to burn low-quality solid fuels in a bed of small particles suspended by a gas stream (usually air that will lift the particles but not blow them out of the vessel. Rapid

burning removes some of the offensive by-products of combustion from the gases and vapors that result from the combustion process.

Fluid-bed combustion is a means for providing high heat transfer rates, controlling sulfur, and reducing nitrogen oxide emissions due to the low temperatures in the combustion zone, which also favor the carbon dioxide equilibrium. Fluidized-bed combustion has the ability to reduce emissions by controlling combustion parameters and by injecting a sorbent, or a pollutant absorbent (such as crushed limestone), into the combustion chamber along with the coal.

In a fluid bed combustor, a gas passed slowly upwards through a bed of solid particles finds its way through the spaces between the particles and the pressure drop across the bed is directly proportional to the flow rate. If the flow rate is increased, a point is eventually reached at which the frictional drag on the particles becomes equal to their apparent weight (i.e., weight minus any buoyancy force); the bed then expands as the particles adjust their positions to offer less resistance to the flow. The bed is now said to be fluidized, and further increase in flow is not accompanied by an increase in pressure drop.

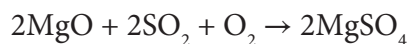
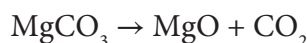
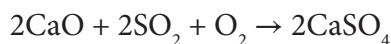
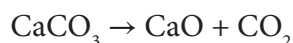
In a fluidized bed, heat and mass transfer between the fluidizing gas and the solid particles are extremely efficient. An additional advantage of fluidized-bed combustors is that they can use fairly coarse feedstock particles (approximately 0.04 in., approximately 1 mm diameter), and there is no need for much of the costly crushing equipment associated with the preparation of pulverized fuel.

A fluid bed combustor usually (in the initial stages) consists of sand or some similar inert material which is fluidized by an air stream and raised to the ignition temperature by an external heating source. When the requisite temperature is reached, the carbonaceous feedstock is fed to the vigorously bubbling bed where it becomes thoroughly mixed with the sand. As combustion begins, volatile material is given off and usually burns in the freeboard above the bed. The solid residue, or char, remains in the bed where the temperature is approximately 900°C (1650°F).

Ash from the carbonaceous feedstock and the residue from any limestone added to remove sulfur, together with the initial sand, are removed from the bottom of the bed, although organic and inorganic particles eventually become small enough to be carried over (entrained) in the flue gases. This fly ash has to be removed before these gases are discharged to the atmosphere; any unburned material represents a significant loss of efficiency, and arrangements are often made for recirculation of the fly ash.

Mechanical problems associated with fluidized combustion are encountered with the feeding of the carbonaceous feedstock and particularly with the withdrawal and separation of the ash from the char or unreacted the carbonaceous feedstock for recycling back to the combustion chamber.

The sulfur may be removed downstream with suitable ancillary controls, but capture during combustion (by adding limestone, CaCO_3 , or dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$) to the bed) may be preferred.



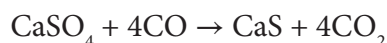
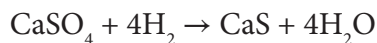
The spent sorbent from fluidized bed combustion may be taken directly to disposal and is much easier than the disposal salts produced by wet limestone scrubbing. These latter species are contained in wet sludge having a high volume and a high content of salt-laden water. The mineral products of fluidized bed combustion, however, are quite dry and in a chemically refractory state, and, therefore, disposal is much easier and less likely to result in pollution.

The spent limestone from fluidized bed combustion may be regenerated thereby reducing the overall requirement for lime and thereby decreasing the disposal problem. Regeneration is accomplished with a synthesis gas (consisting of a mixture of hydrogen and carbon monoxide) to produce a concentrated stream of sulfur dioxide:





The calcium oxide product is supplemented with fresh limestone and returned to the fluidized bed. Two undesirable side reactions in the regeneration of spent lime produce calcium sulfide:



This results in recirculation of sulfur to the bed.

Ash agglomeration is not guaranteed as a means of ready separation and reducing bed carry-over; attrition occurs and particulates occur in the off-gases that require controls.

Combustion in a fluidized bed has some particular benefits including suitability for use with low-grade, high-ash carbonaceous feedstocks and lower bed temperatures compared to those in a conventional furnace. As a result of the lower temperature, the nitrogen oxide levels in the flue gas are reduced considerably.

See also: Combustion.

Fluid-Bed Gasifier

In the fluidized bed gasifier, the fuel is fluidized using oxygen (or air) and steam. The ash is removed dry or as agglomerates. The temperatures are relatively low in dry ash gasifiers, so the fuel must be highly reactive. The agglomerating gasifiers have slightly higher temperatures, and are suitable for less reactive feedstock. Fuel throughput is higher than for the fixed bed, but not as high as for the entrained flow gasifier. The conversion efficiency is rather low, so recycle or subsequent combustion of solids is necessary to increase conversion. Fluidized bed gasifiers are most useful for fuels that form highly corrosive ash that would damage the walls of slagging gasifiers.

See also: Gasification, Gasifiers.

Fluid-Bed Incinerator

The fluidized bed incinerator uses a strong airflow through a sand bed until a point is reached where the sand particles separate to let the air through and mixing and churning occurs; thus, a fluidized bed is created and fuel and waste can now be introduced. The sand with the pre-treated waste and/or fuel is kept suspended on pumped air currents and takes on a fluid-like character. The bed is thereby thoroughly mixed and agitated keeping small inert particles and air in a fluid-like state. This allows all of the mass of waste, fuel, and sand to be fully circulated through the furnace.

The heat produced by an incinerator can be used to generate steam which may then be used to drive a turbine in order to produce electricity. However, the amount of energy produced is very much dependent upon the type and composition of the waste used as the feedstock. Much of the current thinking involves co-incineration of a specified amount of the waste (calculated on the basis of the carbon content of the waste) with, for example, coal to produce a consistent amount of energy.

Incineration has a number of outputs such as the ash and the emission to the atmosphere of flue gas. Before the flue gas cleaning, the flue gases may contain significant amounts of particulate matter, heavy metals, dioxins, furans, sulfur dioxide, hydrochloric acid, and polynuclear aromatic hydrocarbon derivatives (carcinogens).

The most publicized concerns related to the incineration of municipal solid wastes involve the fear that it produces significant amounts of emissions of dioxin derivatives and furan derivatives. These derivatives are considered by many to be serious health hazards. Older-generation incinerators that were not equipped with modern gas cleaning technologies were indeed significant sources of dioxin emissions. However, modern incinerators must limit and even mitigate such emissions.

See also: Incinerators.

Fluid-Bed Processes

In its simplest form, a fluidized bed may be thought of as a vessel containing particulate solid material into which a fluid is introduced. The fluid may be a liquid or a gas. When the fluid flowing at sufficient velocity contacts the solids, a suspension is formed that takes on certain fluid-like properties that the stationary bed of solids by themselves cannot attain. The suspension is termed a fluidized bed. The dynamic flow structure inside a fluidized bed will depend on the velocity of the fluidizing medium, which establishes the regime of fluidization in which the bed operates.

Gas is introduced through a distributor plate at the bottom of the bed. The distributor plate is designed to promote even gas distribution in the bed and to support the weight of the solids at rest.

At low velocities, the solids remain in a packed state. As the gas velocity is steadily increased, a point is reached where the upward force of the gas is sufficient to counteract the downward force of the bed mass and wall friction effects. At this point, the bed unlocks to form a gas-solid suspension. This is known as minimum or incipient fluidization, and the velocity at which it occurs, the minimum fluidization velocity.

The dynamic behavior of a bubbling fluidized may be quantified by fluctuations in bed pressure as measured with pressure transducers. A common plot used in the fluidization literature is the standard deviation of the pressure fluctuation versus gas velocity. The standard deviation increases with increasing velocity to a maximum, after which it decreases and then levels off. The increase in standard deviation is generally interpreted to be the result of the competing mechanisms of bubble coalescence and bubble break-up in the bed that leads to a high degree of variability. Beyond the maximum in standard deviation, bubble break-up dominates and well-defined bubbles are replaced with large voids. This is known as the turbulent regime. The voids rapidly form and disintegrate and move freely throughout the bed. This form of fluidization (i.e., without bubbles) leads to better gas-solid contacting and hence higher conversion in fluidized bed chemical reactors.

At still higher gas velocities, entrainment of the solid phase becomes significant. The solid particles are hence dispersed in the continuous gas phase. This regime of fluidization, known as the fast fluidization regime, is typified by the slip between solids and gas. Slip refers to the relative velocity between the solid and gas phases achieved by the downward-acting force of gravity, counteracting the upward drag force of the gas on the solids. For individual particles, the slip velocity is equal to the terminal settling velocity of a particle. However, it has been observed that the average slip velocity in a fast fluidized bed is an order of magnitude higher than the terminal velocity of a single particle. This has been attributed to the presence of particle clusters that tend to form in this regime of fluidization. The clusters are segregated to the wall where they flow downward, giving rise to high slip.

The final regime of fluidization is pneumatic transport. In this regime, the gas velocity is sufficiently high to transport all of the particles in the upward direction; there is no longer any downflow of solids at the wall. It has been suggested that the flow is dilute in the pneumatic transport regime, but the solid phase can also flow upward at the wall under high-density flow conditions.

Fluid-Bed Reactor

A fluid-bed reactor (fluidized bed reactor) is a type of reactor device that can be used to carry out multiphase chemical reactions. In this type of reactor, a fluid (gas or liquid) is passed through a granular solid material (usually a catalyst possibly shaped as tiny spheres) at high enough velocity to suspend the solid and cause it to behave as though it were a fluid (fluidization).

The solid substrate (the catalytic material upon which chemical species react) material in the fluidized bed reactor is typically supported by a porous plate (distributor). The fluid is then forced through the distributor up through the solid material. At lower fluid velocities, the solids remain in place as the fluid passes through the voids in the material. As the fluid velocity is increased, the reactor will reach a stage where the force of the fluid on the solids is enough to balance the weight of the solid material (incipient fluidization) and occurs at this minimum fluidization velocity and, once the minimum velocity is surpassed, the contents of the reactor bed expand and swirl around much like boiling water and the reactor is now a fluidized bed.

The advantages of fluid-bed reactors are (i) uniform particle mixing (ii) uniform temperature gradient, and (iii) ability to operate in a continuous state. However, as in any design, the fluidized bed reactor does have its drawbacks, such as: (i) increased reactor size, (ii) pumping requirements and pressure drop, (iii) particle entrainment, and (iv) erosion of internal components.

Fluidization can be registered exactly by measuring the pressure drop over the bed as a function of the gas velocity. In a packed bed reactor, the pressure drop increases monotonously with increasing gas velocity. At a minimum fluidization velocity, the increase in the pressure drop stagnates, and at even higher flow values, the pressure drop simply remains at this constant level. The minimum fluidization velocity and bed porosity in minimum fluidization are thus very central criteria in the design of fluidized beds.

Fluid-Bed Thermal Cracking

The first commercial use for fluidized thermal cracking dates back to the 1930s for coal gasification. Like other pyrolysis processes, the fluidized thermal cracking process burns waste with high combustion efficiency; however, it has a few other added advantages. Since it is a fluidized bed process, there is a rapid mixing of solid particles which enables a uniform temperature distribution; thus, the operation can be simply controlled. Fluidization also enhances the heat and mass transfer rates, which in turn, decreases the amount of carbon monoxide emitted.

In the process, a waste feedstock (such as crushed tire chips) is sent to the fluidized bed using a screw feeder. Air heated by a preheating furnace is fed to the reactor bottom in order to elevate the reactor temperature near cracking conditions [400 to 600°C (750 to 1,110°F)] before the chips are introduced. This enables the tire chips themselves to maintain the cracking temperature. A continuous cyclone is used to remove the char. The cracked gases are brought into contact with the recovered oil from the quench tower. Part of the recovered oil is recycled to the quench tower and the remainder sent to an oil storage tank for further purification. The uncondensed gas is sent to a treatment process to remove the hydrogen sulfide.

See also: Thermal Cracking.

Fly Ash

Fly ash is the airborne components of ash produced in combustion processes that use carbonaceous feedstocks, and the fly ash is carried into the atmosphere by flue gases (also referred to as stack gases).

Fly ash contains toxic metals such as arsenic and cadmium. In the United States, the Clean Air Act requires that fly ash be removed from the emissions. As a result, antipollution devices such as air scrubbers, baghouses, and electrostatic precipitators are used to trap these pollutants. Baghouses work like giant vacuum cleaners, drawing emissions through giant fabric bags that trap the fly ash inside. Electrostatic precipitators use discharge electrodes (electrically charged parts of an electric circuit) to trap ash particles.

In an electrostatic precipitator, the electrodes are located between long, positively charged collection plates. As the fly ash passes between these collection plates, the discharge electrodes give each particle a negative charge. These negatively charged particles are then attracted to and held by the positively charged collection plates.

The removal of fly ash from combustion effluent streams is as important to the environment as the removal of sulfur oxides and nitrogen oxides. If not removed, the inorganic constituents and the organic constituents of the ash can cause serious environmental consequences, in addition to the solid particles acting as condensation nuclei and (catalytic) surfaces for the conversion of sulfur dioxide to the trioxide:



Depending upon the source and makeup of the material being burned, the components of fly ash vary considerably. Toxic constituents depend upon the specific feedstock.

Fly ash is composed of small ash particles that are carried in suspension in combustion products. However, depending upon the source and makeup of the material being burned, the components of fly ash vary considerably. Toxic constituents depend upon the specific feedstock.

See also: Combustion, Fly Ash, Incinerator. .

Forage Crop

A forage crop is a crop of cultivated plants or plant parts, other than separated grain, produced to be grazed or harvested for use as feed for animals. The crops that are grown intensively with multiple cuttings per year include three major groups of (i) grasses, including cereals that are harvested green, (ii) legumes, including pulses that are harvested green, and (iii) root crops that are cultivated for fodder.

Furthermore, forage crops (e.g., forage sorghum, Sudan grass) hold promise for ethanol production because, in their early stage of growth, there is little lignin and the conversion of the cellulose to sugars is more efficient. In addition, the proportion of carbohydrates in the form of cellulose is less than in the mature plant.

Forage crops achieve maximum growth in a relatively short period; they can be harvested as many as four times in one growing season. For this reason, forage crops cut as green chop may have the highest yield of dry material of any storage crop.

In addition to cellulose, forage crops contain significant quantities of starch and fermentable sugars which can also be converted to ethanol. The residues from fermentation containing non-fermentable sugars, protein, and other components may be used for livestock feed.

See also: Crops.

Forest Health

Forest health refers to the production of forest conditions which directly satisfy human needs and by resilience, recurrence, persistence, and biophysical processes which lead to sustainable ecological conditions. Thus, forest health refers to a condition of ecosystem sustainability and attainment of management objectives for a given forest area; usually considered to include green trees, snags, resilient stands growing at a moderate rate, and endemic levels of insects and disease.

The health of national forests and grasslands is paramount to our mission of caring for the land and serving people. The Forest Service works to maintain, enhance, and restore healthy forest conditions on the national forests and grasslands.

See also: Forest Land, Forest Residues, Wood.

Forest Land

A forest is an area of land dominated by trees and spanning more than (approximately) 1.2 acres with trees higher than 16 feet and a canopy cover of more than 10%, or trees able to reach these thresholds in situ. Forest trees can be of any size, including land that formerly had such tree cover and that will be naturally or artificially regenerated; includes transition zones, such as areas between heavily forested and non-forested lands with forest trees and forest areas adjacent to urban and built-up lands; also included are pinyon-juniper and chaparral areas; the minimum area for classification of forest land is 1 acre. The six types of forest are: (i) equatorial moist evergreen or rainforest, (ii) tropical deciduous forest, (iii) Mediterranean forests, (iv) temperate broad-leaved deciduous and mixed forest, (v) warm temperate broad-leaved deciduous forest, and (vi) coniferous forest.

Forests filter out pollutants and particulates so that citizens pay less to treat their drinking water. Another way tree-covered landscapes help is by soaking up rainwater, releasing it slowly over time, and reducing the amount of runoff that causes rivers and streams to flood.

See also: Forest Health, Forest Residues, Wood.

Forest Residues

Material not harvested or removed from logging sites in commercial hardwood and softwood stands as well as material resulting from forest management operations such as precommercial thinnings and removal of dead and dying trees.

Forestry residues are produced when controlled thinning of plantations and trimming of felled trees is undertaken to reduce forest fire risk and to accelerate the forest growing rate that can sometimes be prevented if the area is overpopulated. This waste is usually just left to rot on the forest ground; extracting and collecting it clear up the forest making it easily accessible and manageable. In this category, waste from public gardens and woods can also be included. The waste can be collected, dried, and used as fuel.

Young forests sometimes get too dense. Thinning these forests helps the trees to grow into a more valuable and better-quality forest. The fining process can be carried out manually or automatically with wood collectors. The whole tree received from the thinning consists of a small diameter stand wood, branches, leaves, and needles and provides a significant energy potential for solid biofuels.

In most countries, forest slash is still not used whereas in Finland, Sweden, and a couple of other countries, this energy resource is largely utilized. These residues are the main source of forest fuels from the final felling of trees. At the felling areas, for every m³ of solid industrial wood, the residual biomass generated amounts from 35 to 45%. Forest slash mainly consists of the tops of trunks, stems, branches, leaves, stumps, and roots and when discharged can cause environmental problems and the loss of a natural resource. Logging residues can be effectively used with a new bundling technology.

Stumps and roots are a major unexploited resource of forest logging residues. They consist more than 20% of a harvestable dry mass of a tree. In regeneration cuttings, the full yield from stumps has turned to be as high as from aboveground residues. The stump harvesting, handling, and crushing technology is becoming cost competitive, and the quality of these chips meets the requirements set for fluidized bed boilers. Silvicultural works related to removing stumps are becoming easier to handle and cost-effective.

See also: Forest Health, Forest Land, Wood.

Fossil Fuel Resources

Fossil fuels are those fuels, namely, coal, crude oil (including heavy crude oil and extra heavy crude oil, and tar sand bitumen), natural gas, and oil shale are produced by the decay of plant remains over geological time. These fuels are carbon-based and represent a vast source of energy. In fact, at the present time, the majority of the energy consumed by humans is produced from the fossil fuels, coal, crude oil, and natural gas with smaller amounts of energy coming from nuclear and hydroelectric sources.

Planning for the future use of these materials requires (as it does for any resource) an estimate of the amounts of fossil fuels which remain. However, the estimates of the fossil fuels available for future use differ considerably. The issue lies with the use of so-called undiscovered reserves (or reserves-yet-to-be-discovered) of the fossil fuels, but suppositions that there are yet-to-be-discovered reserves of fossil fuels is open to much debate and many questions.

In terms of resource availability, it is a matter of understanding (i) the amount of a resource that is available, (ii) recovery of the resources with the maximal efficiency, and (iii) the application of recovery methods that will cause minimal damage to (disturbance of) the environment. Estimates of the quantities of recoverable fossil fuels in the world vary and are subject to much speculation because of the loose definition of the term resource.

Apart from providing the major source of energy for industrial and domestic consumption, fossil fuels also provide, in many cases, the means (energy) by which other resources can be recovered and converted to products for consumer use. Therefore, it is worthwhile at this point giving consideration to the impact of fossil fuels not only on the evolution of science and engineering (in fact, on the progress of technology in general) but also on the environment with some indication of the steps that will be necessary to ensure reductions in emissions from the use of such fuels (Walker and Wirl, 1994).

First, and to reemphasize, fossil fuels are not the only source of pollutants but they are a major source of energy. As such, the use of fossil fuels has been the cause for considerable criticism but it is not the fuel that is at fault.

It is the manner in which the fuels are used and has been due to lack of environmental-related oversight during the production of energy from the fuel. Thus, it is necessary to reconsider the strategies for fossil fuel use whereupon it may be discovered (again!) that fossil fuels can be used in an environmentally acceptable manner. Hence, it is necessary to understand, by way of background, the various types of fossil fuels that generate energy and the evolution of their use in this present time. This will also aid in understanding the means by which fossil fuels can produce noxious emissions. Such an understanding will then lead to means by which the emissions can be reduced, if not eliminated completely.

In summary, understanding the nature of fossil fuels and their recovery from the formation in which they exist can be equated to the recovery of any mineral and its use as a commodity. There is also the need to understand the influence of the various processes on the ecological cycles as well as, in many cases, the potential for the production of acid rain and the potential for global warming, or any similar effect.

Thus, understanding the resource is a benefit to an understanding the recovery processes and the conversion processes through an evaluation of the products and the effects on the environment of the recovery process and manufacture of the products.

See also: Biogeochemical Cycles.

Fouling

Fouling is the accumulation of small, sticky molten particles of ash on a boiler surface. It is the buildup that occurs in the lower temperature regions of the combustion system. It affects the design and maintenance of superheaters, reheaters, and furnace water walls. Fouling has been found to be related to the alkaline content of ash, although the total quantity of alkali is not necessarily an accurate index of fouling potential. Sodium in ash has been found to be a key link in the fouling formation. Specifically, the vapor-phase sodium in the combustion gases promotes contact and subsequent bonding between ash particles and metal surfaces as gas cools and the sodium condenses. The high-alkali ash found in many biomass feedstocks has been linked to a rapid buildup of deposits, which influences the design of tube spacing in convective passes.

Ash is composed mostly of metal oxides, and the composition affects the softening point. Iron oxides are a particular source of problems, and the reducing atmosphere ($\text{CO} + \text{H}_2$; produced by the water gas reaction) in the fuel bed serves to reduce ferric oxide (Fe_2O_3) to ferrous oxide (FeO) with the production of clinker which will contribute to reactor fouling.

In addition, the fouling of combustion systems has also been related to the alkali metals content of the carbonaceous feedstock. For example, a carbonaceous feedstock with a total alkali metal content $<0.5\%$ w/w (as equivalent sodium oxide, Na_2O) produces deposits that can be removed by the action of soot blowers (perforated lances through which jets of high-pressure air or steam can be sent between boiler tubes), but for the carbonaceous feedstock having more than 0.6% w/w alkali metal (as equivalent sodium oxide), the deposits increased markedly and can be a major problem.

To combat fouling, modern combustion equipment is designed to ensure that particles are cooled to well below their fusion temperatures before they can reach the banks of closely spaced tubes in the upper regions of the boiler. In pulverized fuel systems, provision is usually made for tilting the burners and thereby periodically altering the heat regime. In addition, tube deposits are routinely dislodged by frequent soot blowing.

See also: Fouling Tendency.

Fouling Tendency

Fouling tendency is the potential for a fuel to form unwanted insoluble deposits during the course of its operation. Usually, the deposits are carbonaceous in nature. These deposits, in turn, can degrade system performance by causing less efficient heat exchange, plugging, and other problems, which may ultimately lead to system failure. All fuel systems are subject to some degree of fouling. Some fuel systems addressed in this article are (i) military aircraft,

(ii) drop tube furnaces, (iii) fluidized bed combustors, (iv) solid fuel combustors, (v) biomass boilers, and (vi) ethylene furnaces.

Fouling tendency is unique to each fuel system and is dependent on a variety of factors which are of varying importance from system to system. In addition, each system may experience different fouling mechanisms in different parts of the system. Some factors that influence fouling tendency include (i) the chemical properties and reactivity of the fuel used in the system operation, (ii) the design of the system, temperature, (iii) the heat flux, materials comprising the system, (iv) the pressure, (v) the flow rate and residence time, (vi) the size of particles in the fuel, and (vii) the length of time the system is operated.

The fouling tendency of a fuel is dependent on the unique chemistry of the fuel used in the system. In the case of most jet fuels, for example, alkanes and aromatics are the major components of the fuel, but trace amounts of polar species in the fuel containing oxygen, nitrogen, and or sulfur have the greatest effect on fouling. Fouling is also influenced by the presence of low levels of dissolved metals in the fuel. These metals typically act as initiators in the fuel's free radical chemistry, ultimately leading to faster formation of deposits. In jet fuel, the deleterious effect of copper is especially noteworthy. In a drop tube furnace, alkali and alkali-earth elements, especially sodium, have been linked to fouling. The presence of gases, such as dissolved oxygen, in the fuel also has an important effect on fouling. The presence of oxygen is related to the fouling process, though the total amount of deposit produced from this free radical process is fuel dependent. In fluidized bed combustion, the chemical makeup of the fuel, be it peat, forest residue, or willow, greatly influences fouling processes. Also, the age of the fuel has some bearing on its fouling tendency. An older fuel will typically have had more time to chemically react with its solid, liquid, and/or gaseous environment, and hence may pick up elements, such as minerals, which encourage fouling. This is true for FBC boiler fuels studied.

Fuel systems are often designed with the fouling tendency of a typical system fuel in mind. Where and when fouling will occur is dependent in part on an individual system's geometry. A change in flow direction or diameter, or any change in flow path in the system may influence the location of surface deposits. Fouling tends to reliably occur in certain parts of a given system. In a drop tube furnace studied, for example, fouling often occurred in the convective section. For a flowing system, a small opening for flow will generally result in more detrimental fouling problems—i.e., plugging—than a large opening. In aircraft, for example, the spray nozzle openings are small and blockage or change of the spray pattern due to partial plugging are important problems.

The temperature at which reactions occur is also important to fouling tendency. In many but not all cases, the higher the temperature, the worse fouling becomes. However, the amount of time the fuel is exposed to a given temperature and the amount of dissolved oxygen available greatly influence the effect of temperature on fuel fouling. Because of this, a particular flow path at a given temperature may equal a faster rate of fouling than another flow path at that temperature. For example, a military fighter aircraft at idle conditions will experience more fuel recirculation, which may form more deposition precursors and speed up the fouling process, than in the case where the aircraft is at full thrust. Also, cooling, especially an abrupt cooling, may encourage deposits to fall out, increasing the fouling tendency of a given system. This is true for a biomass boiler studied.

The fouling tendency of the fuel in a particular system is also dependent on the materials which comprise the system. Fuel in contact with different kinds of metals may produce different amounts of surface deposition. Also, fuel in contact with a surface that is more chemically inert, such as with a polysiloxane layer, will produce considerably fewer deposits than a fuel that is in contact with a more chemically active surface, such as a metal one.

Increasing pressure in a fuel system may or may not increase fouling. Whether pressure has an effect on fouling seems to depend on other specific reaction conditions, such as temperature and residence time. The effect of pressure probably has the most to do with whether a system is completely pyrolytic or not (that is, the entire reacting fuel and wall are at 300°C or greater), and whether dissolved oxygen is still present in the fuel. Some systems are more sensitive to pressure effects than others. For example, systems which produce gas, such as ethylene furnaces, typically experience an increase in fouling with increased pressure.

Generally, the lower the flow rate of the system, the greater the fouling tendency. For instance, systems using crude oil, atmospheric tower bottoms, and vacuum tower bottoms are subject to greater fouling with slower flow. The amount of fouling is dependent on the amount of time a fluid stays in a reaction zone. This time of occupation is called residence time. Flow rate is inversely proportional to residence time. The longer the fluid resides in the reaction zone, the more reaction will occur and the greater the deposition will be for the fuel.

The greater the size of the particles in the fuel flow, the greater the fouling tendency of the fuel tends to be. Large particles can be present in the unstressed fuel, contributing to fouling by plugging injectors or filters more easily, or large particles can be made during thermal stressing of the fuel. In the latter case, small particles in the fuel of the same type can stick to one another and form larger particles, and these in turn stick together and eventually form a mass of solid matter which becomes a layer of deposit on the wall. This type of deposit, usually made of a number of aromatic molecules joined together, is often referred to as soot. If this process is inhibited, for example by addition of a dispersant additive which prevents particle growth, significantly less fouling will typically be observed. Particle size also can affect where and when fouling occurs.

See also: Fouling.

Fractional Composition

The fractional composition of a fuel or a fuel source is the composition as determined by fractionation (separation) methods. The methods usually involve the separation of crude oil into two-to-five bulk fractions. The general procedure is to employ techniques that segregate the constituents according to molecular size and molecular type.

Various analytical techniques have been developed for the identification and quantification of every molecule in the lower boiling fractions of crude oil, and, as a result, it is recognized that the name crude oil does not describe a composition of matter but rather a mixture of various organic compounds that includes a wide range of molecular weights and molecular types that exist in balance with each other.

The fractional composition of crude oil varies markedly with the method of isolation or separation, thereby leading to potential complications (especially in the case of the heavier feedstocks) in the choice of suitable processing schemes for these feedstocks. Crude oil can be fractionated into three or four general fractions: (i) the asphaltene fraction, (ii) the resin fraction, (iii) the aromatics fraction, and (iv) the saturates fraction. Thus, it is possible to compare inter-laboratory investigations and thence to apply the concept of predictability to refining sequences and potential products.

Investigations of the character of crude oil through fractionation studies has been practiced since at least 1837, although modern fractionation techniques are essentially a twenty-first century approach to examining crude oil composition.

The success of any attempted fractionation procedure involves not only the application of one particular technique but also the utilization of several integrated techniques, especially those techniques involving the use of chemical and physical properties to differentiate among the various constituents. For example, the standard processes of physical fractionation used in the crude oil industry are those of distillation and solvent treatment, as well as adsorption by surface-active materials. Chemical procedures depend on specific reactions, such as the interaction of olefins with sulfuric acid or the various classes of adduct formation. Chemical fractionation is often but not always successful because of the complex nature of crude oil. This may result in unprovoked chemical reactions that have an adverse effect on the fractionation and the resulting data. Indeed, caution is advised when using methods that involve chemical separation of the constituents.

The order in which the several fractionation methods are used is determined not only by the nature and/or composition of the crude oil but also by the effectiveness of a particular process and its compatibility with the other separation procedures to be employed. Thus, although there are wide variations in the nature of crude oil, there have been many attempts to devise standard methods of crude oil fractionation. However, the various laboratories are inclined to adhere firmly to, and promote, their own particular methods. Recognition that no one particular method may satisfy all the requirements of crude oil fractionation is the first step in any fractionation study. This is due, in the main part, to the complexity of crude oil not only from the distribution of the hydrocarbon species but also from the distribution of the heteroatom (nitrogen, oxygen, and sulfur) species.

See also: Fractionation.

Fractionation

The composition of any feedstock or products, including those involved as alternative fuel sources, is an important aspect in determining the suitability of the feedstock for the process and the importance of the process in producing

the desirable products. In addition, the order in which the several fractionation methods are used is determined not only by the nature and/or composition of the feedstock (such as a complex material such as bio-oil) but also by the effectiveness of a particular process and the compatibility of the fractionation process with the other separation procedures to be employed. For example, rather than leaving the further processing of gaseous, liquid, or solid products to guesswork, determining the composition of the feedstock and the associated product before submitting the feedstock to a conversion process is a valuable asset in determining the suitability of the process.

The importance of chemical and physical properties is dependent upon the composition of the feedstock. In the strictest sense, feedstocks such as biomass and waste, are complex chemical mixtures which contain hydrocarbon derivatives and non-hydrocarbon derivatives that confer properties on the mixture that may not be reflected in the composition. Therefore, it is necessary to apply various test methods to petroleum and petroleum products to determine if the material is suitable for processing and (in the case of the products) for sale with a designated use in mind.

In fact, the processes that constitute gas cleaning operations are derived from the various gas cleaning options and may, in fact, be considered as the application of a series fractionation processes to the fractionation of a gas stream into a series of sub-fractions or products. Also, the order in which any one of the several fractionation methods are used is determined not only by the nature and/or composition of the feedstock or product(s) oil but also by the effectiveness of a particular process and its compatibility with the other separation procedures to be employed. Thus, although there are wide variations in the nature of feedstocks (especially biomass) for the production of alternative fuels, the recognition that no one particular method may satisfy all the requirements of the fractionation process is the first step in any fractionation study. This is due, in the main part, to the complexity of the feedstock not only from the distribution of the constituents of the feedstock species but also from the distribution of the heteroatom (nitrogen, oxygen, and sulfur) species and the occurrence of these species in the product(s).

See also: Bio-oil, Fractional Composition, Gas Cleaning, Gas Processing, Gas Treating.

Fractionation – Absorption Methods

Already used in gas cleaning processes, absorption methods offer fractionation method in the gas cleaning (gas processing industry).

Gas processing (gas refining) is a pertinent example of the application of fractionation methods to the determination of the composition of a gaseous feedstock or the distribution of gaseous products from a process.

Many chemical processes are available for processing or refining natural gas. However, there are many variables in the choice of process or the choice of refining sequence that dictate the choice of process or processes to be employed. In this choice, several factors must be considered: (i) the types and concentrations of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide and carbon dioxide, the gas stream may contain other contaminants, such as mercaptans (also called *thiols*, R-SH) and carbonyl sulfide (COS). In fact, the variation in the composition of the gases that require separation either before being assigned to further use requires a variation of separation types to ensure that specifications are met and the environment is protected. The presence of various constituents may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to separate large amounts of acid gases.

Method selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes separate both hydrogen sulfide and carbon dioxide from a gas stream while other methods may be designed to remove hydrogen sulfide only. It is important to consider the process method for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

Fractionation – Adsorption Methods

Separation by adsorption chromatography essentially commences with the preparation of a porous bed of finely divided solid, the adsorbent. The adsorbent is usually contained in an open tube (column chromatography); the sample is introduced at one end of the adsorbent bed and induced to flow through the bed by means of a suitable solvent. As the sample moves through the bed, the various components are held (adsorbed) to a greater or lesser extent depending on the chemical nature of the component. Thus, those molecules that are strongly adsorbed spend considerable time on the adsorbent surface rather than in the moving (solvent) phase, but components that are slightly adsorbed move through the bed comparatively rapidly.

It is essential that, before application of the adsorption technique to the feedstock, any insoluble material should be completely removed. The prior removal of an insoluble portion of the feedstock is essential insofar as the insoluble constituents may be irreversibly adsorbed on the adsorbent.

Careful monitoring of the experimental procedures and the nature of the adsorbent has been responsible for the successes achieved with this particular technique. Early procedures consisted of warming solutions of the feedstock with the adsorbent and subsequent filtration. This procedure has continued to the present day, and separation by adsorption is used commercially in plant operations in the form of clay treatment. In addition, the proportions of each fraction are subject to the ratio of adsorbent to the liquid feedstock.

It is also advisable, once a procedure using a specific adsorbent has been established, that the same type of adsorbent be employed for future fractionation since the ratio of the product fractions varies from adsorbent to adsorbent. It is also very necessary that the procedure be used with caution and that the method not only be reproducible but quantitative recoveries and reproducibility be guaranteed.

In summary, the variety of fractions isolated by these methods and the potential for the differences in composition of the fractions make it even more essential that the method is described accurately and that it is reproducible not only in any one laboratory but also between various laboratories.

Fractionation – Chemical Methods

Methods of fractionation using chemical reactants are entirely different in nature from the methods described in the related sections. Although several methods using chemical reactants have been applied to fractionation, methods such as adsorption, solvent treatment, and treatment with alkali are often applied to product purification as well as separation.

The method of chemical separation commonly applied to separate a feedstock into various fractions is treatment with sulfuric acid, but caution is advised because of the potential for the formation of complex sulfates and difficult-to-break emulsions. Obviously, the success of this fractionation method is feedstock dependent and, in conclusion, it would appear that the test be left more as a method of product cleaning for the process has been widely used in industry rather than as a method of separation of the various fractions.

Fractionation – Distillation Methods

Distillation is a means of separating chemical compounds (usually liquids) through differences in the vapor pressure of the various liquids.

Simple distillation is effective only when separating (under the conditions of the method) a volatile liquid from a nonvolatile substance or when separating liquid constituents that differ in boiling point. Thus, in the mixture, the components evaporate and the vapor has a composition determined by the chemical properties of the mixture. Distillation of a given component is possible, if the vapor has a higher proportion of the given component than the mixture. This is caused by the given component having a higher vapor pressure and a lower boiling point than the other components.

The equipment may affect separation by one of two main methods. First, the vapors given off by the heated mixture may consist of two liquids with significantly different boiling points. Thus, the vapor that is given off is in the vast majority of one or the other liquid, which after condensation and collection effects the separation. Second, fractional distillation may be necessary and is more effective at separating liquids that have similar boiling points. This method relies upon a gradient of temperatures existing in the condenser stage of the equipment. Often in this technique, a vertical condenser, or column, is used, and by removal of the distillation products that are liquid at different heights up the column, it is possible to separate liquids that have different boiling points. The greater the distance over which the temperature gradient in the condenser is applied leads to easier and more complete separation.

The basic idea behind fractional distillation is the same as simple distillation, only the process is repeated many times. If simple distillation was performed on a mixture of liquids with similar volatilities, the resulting distillate would be more concentrated in the more volatile compound than the original mixture, but it would still contain a significant amount of the higher boiling compound. If the distillate of this simple distillation was distilled again, the resulting distillate would again be even more concentrated in the lower boiling compound, but still a portion of the distillate would be the higher boiling compound. If this process is repeated several times, a fairly pure distillate will eventually result.

In fractional distillation, the vapors formed from the boiling mixture rise into the fractionating column where they condense on the column's packing. This condensation is tantamount to a single run of simple distillation; the condensate is more concentrated in the lower boiling compound than the mixture in the distillation flask. As vapors continue to rise through the column, the liquid that has condensed will vaporize. Each time this occurs, the resulting vapors are more and more concentrated in the more volatile substances. The length of the fractionating column and the material it is packed with impact the number of times the vapors will condense before passing into the condenser; the number of times the column will support this is referred to as the number of theoretical plates of the column.

The fractionating column supplies a temperature gradient over which distillation occurs. In an ideal situation, the temperature in the distillation flask would be equal to the boiling point of the mixture of liquids and the temperature at the top of the fractionating column would be equal to the boiling point of the lower boiling compound; all of the lower boiling compound would be distilled away before any of the higher boiling compound. In reality, fractions of the distillate must be collected because as the distillation proceeds, the concentration of the higher boiling compound in the distillate being collected steadily increases. Fractions of the distillate, which are collected over a small temperature range, will be essentially purified; several fractions should be collected as the temperature changes, and these portions of the distillate should be distilled again to amplify the purification that has already occurred.

Fractionation – Solvent Methods

Solvent methods achieve fractionation on the basis of (i) molecular weight and (ii) polarity. A common solvent separation process used involves solvent precipitation. The simplest application of solvent extraction consists of mixing the feedstock with a liquid, which results in the formation of two phases. This causes distribution of the feedstock constituents over the two phases: (i) the dissolved portion, which is the extract and (ii) the non-dissolved portion, which is the raffinate.

The list of compounds that have been suggested as selective solvents for the preferential extraction fractionation of the variety of feedstocks contains a large selection of different functional types. However, before any extraction process is attempted, it is necessary to consider the following criteria: (i) the differences in the solubility of the feedstock constituents in the solvent should be substantial, (ii) the solvent should be significantly less dense or denser than the product to be separated to allow easier countercurrent flow of the two phases, and (iii) separation of the solvent from the extracted material should be relatively easy. It may also be advantageous to consider other properties, such as viscosity, surface tension, and the like, as well as the optimal temperature for the extraction process.

There is also the option of reactive extraction in which the insoluble feedstock reacts with the solvent at high temperature (which will be dependent on the feedstock composition and properties, the contact time, and the pressure) to produce a soluble product.

Fuel Cell

A fuel cell is an electrochemical device that will efficiently convert diverse fuels directly into electricity without combustion, and they are key elements of a broad portfolio for building a competitive, secure, and sustainable clean energy economy. The fuel cell offers a broad range of benefits, including reduced greenhouse gas emissions; reduced oil consumption; expanded use of renewable power (through the use of hydrogen derived from renewable resources as a transportation fuel as well as for energy storage and transmission); highly efficient energy conversion; fuel flexibility (use of diverse, domestic fuels, including hydrogen, natural gas, biogas, and methanol); reduced air pollution, criteria pollutants, water use; and highly reliable grid support. Fuel cells also have numerous advantages that make them appealing for end users, including quiet operation, low maintenance needs, and high reliability. Because of their broad applicability and diverse uses, fuel cells can address critical challenges in all energy sectors: commercial, residential, industrial, and transportation.

A fuel cell and a battery are both electrochemical devices that convert chemical energy into electrical energy. The chemical reaction in a battery releases electrons that travel between the terminals and out as electricity. Moreover, when electricity is released from the battery, the battery's stored energy is being used up because the battery is a closed storage system. It can only produce so much energy before it dies and needs to be recharged or replaced. The fuel cell, on the other hand, is more of an energy converter than an energy storage device. Its chemical reaction converts hydrogen and oxygen into water and in the process produces electricity. A fuel cell will provide power as long as it is supplied with fuel. It does not run down or require recharging like a battery. A fuel cell can be refilled with hydrogen like filling an automobile gas tank.

Fuel Oil

Fuel oil is produced in a refinery but can also be produced from liquid produced from biomass.

No. 1 fuel oil is a petroleum distillate that is one of the most widely used of the fuel oil types. It is similar to kerosene and is used in burners where vaporization before burning is usually required and a clean flame is specified.

No. 1 fuel oil is used in atomizing burners that spray fuel into a combustion chamber where the tiny droplets burn while in suspension. It is also used as a carrier for pesticides, as a weed killer, as a mold release agent in the ceramic and pottery industry, and in the cleaning industry. It is found in asphalt coatings, enamels, paints, thinners, and varnishes. No. 1 fuel oil is a light petroleum distillate (straight-run kerosene) consisting primarily of hydrocarbons in the range C_9 - C_{16} . Fuel oil #1 is similar in composition to diesel fuel; the primary difference is in the additives.

See also: Refining.

No. 2 fuel oil, also called domestic heating oil or industrial heating oil, is a petroleum distillate that has properties similar to diesel fuel and heavy jet fuel. It is used in burners where complete vaporization is not required before burning. Domestic fuel oil is usually lower boiling and a straight-run product. It is used primarily for home heating. The industrial-grade industrial distillate is a cracked product or a blend of both and is used in smelting furnaces, ceramic kilns, and packaged boilers. No. 2 fuel oil is characterized by hydrocarbon chain lengths in the C_{11} - C_{20} range. The composition consists of aliphatic hydrocarbons (straight chain alkanes and cycloalkanes) (64%), 1-2% unsaturated hydrocarbons (alkenes) (1 to 2%), and aromatic hydrocarbons (including alkyl benzenes and 2-ring, 3-ring aromatics) (35%) but contains only low amounts of the polycyclic aromatic hydrocarbons (<5%).

No. 4 fuel oil is a light (relatively low boiling) industrial heating oil and is used where preheating is not required for handling or burning; there are two grades of No. 4 fuel oil, differing in safety (flash point) and flow (viscosity) properties. No. 5 fuel oil is a heavy (relatively high boiling) industrial fuel oil which requires preheating before burning.

No. 6 fuel oil (also called Bunker C oil or residual fuel oil) is the residuum from crude oil after naphtha-gasoline, No. 1 fuel oil, and No. 2 fuel oil have been removed. No. 6 fuel oil can be blended directly to heavy fuel oil or made into asphalt. Residual fuel oil is more complex in composition and impurities than distillate fuels. Limited data are available on the composition of No. 6 fuel oil. Polycyclic aromatic hydrocarbons (including the alkylated derivatives) and metal-containing constituents are components of No. 6 fuel oil. Preheating is always required for burning this oil.

See: Refining.

Fuels

A fuel is a substance that may be burned in air (or any other oxidant-containing substance) (Table F-7), and the reaction (with the oxidant, for the most part, oxygen) is rapid so that heat and light are emitted in the form of a sustained flame.

Table F-7 General description of fuel types.

Fuel type	Description
Gas	Natural gas, oil derivatives (LPG), acetylene, manufactured gas from coal or oil residue, and biogas from manure or sewage.
Liquid	Crude-oil derivatives (gasoline, diesel, fuel oil), alcohols, ethers, esters, but also liquefied petroleum gas (LPG) at low temperatures.
Solid	Coal (mineral), charcoal (from wood) and biomass (wood, dung), but also waxes, metals, and nonmetals (for example, sulfur ignites easily, producing a pungent blue flame).
	Also, aluminum particles are used in the rocket boosters for heavy-lift payloads.

Fuels are mostly used as convenient energy stores because of their high specific energy release when burnt with omnipresent ambient air (or other specific oxidizer). The same fuel substance may be also used as a feedstock in chemical synthesis (e.g., polymers from petroleum), lubricants, paints (who has never used a coal chunk to draw), and so on, but these uses are minority. Primary fuels (natural fuels) may be difficult to find, and secondary fuels (artificial fuels) may be difficult to manufacture but fuels are easy to store, transport, and use, with the only nuisance of safety (uncontrolled combustion) and pollution (toxic emissions during storage and when burnt).

Although the chemical reactions of wood in air, animal-fat in air, coal in air, natural gas in air (approximated by $\text{CH}_4/\text{O}_2/\text{N}_2$), hydrogen in oxygen (H_2/O_2), silicon in oxygen (Si/O_2), sodium in chlorine ($\text{Na(s)}/\text{Cl}_2(\text{g})$), zirconium powder in carbon dioxide (Zr/CO_2), and nitrocellulose $[-(\text{C}_6\text{H}_{10}\text{O}_5)_n-$ with $n=300$ to $.2000$) in any medium are all of the same chemical type (self-propagating highly-exothermic re-dox reactions, i.e., combustion processes). Usually, the terms words and combustion only refer to easily flammable substances in air (air is the oxidizer or oxidant that is needed by a fuel to burn).

Oxygen in the air is the basic oxidant for fuels: nitrogen is basically inert, although it combines endothermically with oxygen at high temperatures to get the unwanted nitrogen oxide (NO_x) pollutants. Oxygen is readily available from the atmosphere of the Earth.

See also: Gaseous Fuels, Liquid Fuels, Solid Fuels.

Fuels from Biomass

The production of fuels from biomass (biofuels) to replace crude oil and natural gas is in active development, focusing on the use of cheap organic matter (usually cellulose, agricultural, and sewage waste) in the efficient production of liquid and gas biofuels which yield high net energy gain.

The carbon in biofuels was recently extracted from atmospheric carbon dioxide by growing plants, so burning it does not result in a net increase of carbon dioxide in the atmosphere of the Earth. As a result, biofuels are seen by many as a way to reduce the amount of carbon dioxide released into the atmosphere by using them to replace non-renewable sources of energy.

Gasoline is a blend of hydrocarbon derivatives with some contaminants, including sulfur, nitrogen, oxygen, and certain metals. Ethanol and methanol are biofuels that provide an alternative to gasoline. Bioethanol is a fuel produced by processing familiar and renewable crops such as cereals, sugar beet, and maize using natural fermentation. Blended with petrol at 10%, bioethanol can be used in vehicles without the need to change fuel or engine specifications.

Biofuels are important because they replace crude oil fuels and can be used to fuel vehicles, but can also fuel engines or fuel cells for electricity generation. Biofuels are generally more environmentally benign than traditional fuels and are further defined as being renewable, meaning that the feedstock used to make a particular biofuel can be replenished at a rate equal to or faster than the rate at which the biofuel is consumed.

See also: Biodiesel, Ethanol, Gasoline Methanol.

Fuels from Crops

Crops have essentially many functions and benefit particularly for the human animal! Their products are not only used as a primary source of human foods and animal feed, but also as a source of timber, fibers and biomass energy. In addition, crops also have an essential function to maintain ecological systems and natural environment.

Grain crops include corn, wheat, rice, barley, and other cereals. The seeds of these plants are typified by their high starch content that can be hydrolyzed to fermentable sugars for ethanol production. Sugar crops, including sugar cane, beet, and sweet sorghum, are preferable to starch crops to the extent that sucrose is more readily hydrolyzed to fermentable sugars. However, sugar cane production is restricted to warm climates, and requires both high-quality land and irrigation. Sweet sorghum has considerable advantages over sugar cane as an energy crop. It can grow in a variety of soils and climatic conditions, and its production costs have been estimated to be just over half those for sugar cane.

Most of crop production is used as foods, and the concern is that biofuels can consume these crops. However, more crops are being cultivated for non-food use such as pharmaceutical and nutritional products, chemical derivative products such as adhesive, paints, polymer, plastics and industrial oils in forms of bio diesel, ethanol, two cycle oils, transmission fluids, and lubricants.

Many efforts have been carried out to grow crops for food production in order to strengthen food security, and to alleviate the hunger and poverty particularly in developing countries. However, attention should also be directed toward cultivation of crops for non-food use since, in some cases, cultivating for non-food products may provide a higher value added, a higher profit, and higher income, i.e., an increase in farm income. The hunger and poverty problems do not essentially rely on the incapability of individuals to produce of foods by themselves, but depend on the capability of individuals to access foods by their income.

Energy crops are plants grown specifically for use as a fuel. Although growing crops for fuel dates from medieval times, in their modern form, energy crops are the most recent and innovative renewable energy option. Energy crops are important as a renewable energy technology because their use will produce a variety of economic, environmental, and energy benefits.

Wood is the oldest fuel known to man. Burning wood rather than fossil fuels can reduce the carbon dioxide emissions responsible for global climate change. Wood fuel is carbon dioxide neutral. It gives off only as much carbon dioxide when burnt as it stores during its lifetime. In addition, wood fuel has low levels of sulfur, a chemical that contributes to acid rain.

Biomass like wood can be used to produce electricity by direct combustion or gasification. It includes short rotation coppice and forestry waste. Biomass has some attractions as a fuel over some other renewable energy sources since it is not an intermittent resource – it can be supplied on a continuous basis to fuel base load plants.

Regularly coppiced plantations will actually absorb more carbon dioxide than mature trees – since carbon dioxide absorption slows once a tree has grown. Growing crops for fuel, particularly wood coppice, offers very promising developments for the future. Short rotation arable coppicing, using fast-growing willows, is currently seen as an important source of fuel for electricity generation. The overall process involves several stages – growing over two or three years, cutting and converting to wood chip, storage and drying, and transporting to a power plant for combustion. And the combustion process can be very efficient, given the development of advanced co-generation techniques.

Energy crop fuel contains almost no sulfur and has significantly less nitrogen than fossil fuels; therefore, reductions in sulfur oxide and nitrogen oxide pollutants causing acid rain and smog may be realized.

Burning fossil fuels removes carbon that is stored underground and transfers it to the atmosphere. Burning energy crops, on the other hand, releases carbon dioxide, but as their growth requires carbon dioxide, there is no net release of carbon into the atmosphere, i.e., it creates a closed carbon cycle. Furthermore, where energy crops are gasified,

there is a net reduction of carbon dioxide. In addition, substantial quantities of carbon can be captured in the soil through energy crop root structures, creating a net carbon sink.

An additional environmental benefit is in water quality, as energy crop fuel contains less mercury than coal.

Also, growing energy crops on agricultural land that might otherwise be converted to residential or industrial use will reduce erosion/chemical runoff and enhance wildlife habitat. This will give energy producers, and consumers will have available a renewable energy option with uniquely desirable characteristics. For example, energy crops differ from other sources of renewable energy in virtue of the fact that they can be grown to meet the needs of the market whereas other renewable resources (for example, wind and wave power) must be harnessed where and when they occur.

Moreover, the security of energy supply will be significantly enhanced for many crop-growing countries. Energy crop production and use could reduce dependency on imported oil, although complete energy independence must, for the time, remain a possible future event.

See also: Biofuels, Biomass, Crops.

Fuels from Waste

Many fuels can be derived from waste such as (i) waste vegetable oil, (ii) organic waste, and (iii) used tires. Waste vegetable oil currently used to produce biodiesel consists mostly of rapeseed oil; the transesterification process of rapeseed oil produces RME (rape methyl ester). However, there is no guarantee of the purity of the oil as a proportion will be oil produced from other crops such as sunflower oil or olive oil.

Anaerobic digestion is the use of bacteria to decompose organic matter in the absence of oxygen to produce gases. These gases are produced from organic wastes such as livestock manure and food processing waste. The end product is a medium heating value biogas mixture (usually 60% methane, 40% carbon dioxide) and a mixture of solid and liquid fertilizer. Because anaerobic digestion does not produce anymore carbon dioxide than would normally be produced from the wastes' natural decomposition, it is said to be carbon neutral.

There are a number of various designs of digester, but the same process is usually followed. The digester itself comprises of an airtight container with an expandable cover to allow gas buildup before siphoning. Waste is then pumped regularly (typically, once a day) into the digester, remaining there for between 10 and 40 days. The temperature inside the digester must be between 30 and 70 degrees Celsius.

Any mixture of organic waste materials may be used such as animal and human sewage, crop residues, newspaper, abattoir waste, food processing, and agricultural waste. The availability of different feedstocks varies due to different harvest times and also the time of year (e.g., manure collection easier when animals are indoors for winter). Therefore, feedstock mixtures may vary at different times of the year in order to keep the digester active for continuous production.

Since the product in this process is a gas, then generally, this fuel is more suited to electricity generation as opposed to use as a transport fuel. The changes to current infrastructure that would be required to accommodate such a fuel would be difficult at best, though some of the infrastructure does exist due to the use of compressed natural gas (CNG).

Used tire pyrolysis is another process which produces gases, small quantities of liquid, and a solid residue containing carbon and ash. The gases produced in the process can then be used to provide the heating energy for continuing the process. The tire pyrolysis process essentially returns the high heating value of the rubber and oils that were initially used in the manufacture of the tires. By carefully controlling the temperature, pressure, and oxygen level, more pyrolysis oil and charcoal are encouraged. This pyrolysis oil can then be used as a replacement diesel fuel.

A significant number and variety of organic wastes are combusted in energy recovery systems including municipal solid waste (MSW), various forms of refuse-derived fuel produced from municipal solid waste as well as a broad range of other specific specialty wastes. The practice of incinerating waste has become increasingly prevalent in order to accomplish disposal in a cost-effective, environmentally sensitive manner. Combustion of such wastes reduces the volume of material which must be sent to a landfill, reduces the airborne emissions resulting from plant operations and landfill operations, and permits some economic benefit through energy recovery.

The technologies used to combust wastes depend on the form and location of components to be burned. The issues associated with energy generation from waste include fuel composition characteristics, combustion characteristics, formation and control of airborne emissions including both criteria pollutants and air toxics, such as trace metals; and the characteristics of bottom and fly ash generated from waste combustion.

The concept of the incineration of domestic and industrial waste to gaseous fuels is one of the first suggestions from the disposal of waste and the generation of energy. With this in mind, waste incineration has been, and continues to be, practiced in many parts of the world. In fact, co-combustion of waste in (large and efficient) coal-fired power plants is an especially attractive option because of the high conversion efficiency of these plants. However, there are issues that need attention, and while it is not intended here to use the following comments to be a critique of waste incineration, here are lessons to be learned and changes to be made in this manner of waste removal.

Although not in keeping with the main context of this text, i.e., the production of fuels, the incineration of wastes is worthy of mention insofar as waste combustion (although the main goal of incineration is volume reduction with the sterilization of the waste as a significant side-effect) can be a source of energy but, generally. Thus, the incineration process may also be used to produce steam and electricity. However, as the moisture content of the waste increases, a self-sustaining combustion process is not possible. Nevertheless, domestic waste and industrial waste are feedstocks for incinerators.

Incineration is recognized as a waste treatment technology for disposal of the organic constituents of the waste. Incineration and other high-temperature waste treatment systems convert the waste into ash, flue gas, particulate matter, and heat, which can in turn be used to generate electricity. The flue gases are cleaned for pollutants before it is dispersed in the atmosphere. Furthermore, incineration with energy recovery is one of several waste-to-energy technologies such as gasification and anaerobic digestion.

Modern incinerators reduce the volume of the original waste by 95-96%, depending upon the composition and degree of recovery of materials such as metals from the ash for recycling. While incineration does not replace land-filling, it does reduce the necessary volume significantly. In fact, incineration has particularly strong benefits for the treatment of certain waste types in niche areas such as clinical wastes and certain hazardous wastes where pathogens and toxins can be destroyed by high temperatures.

Incineration is not a complete method of disposal; the main advantage of the process is that a residue is produced which is substantially reduced in volume and may be relatively inert. In addition, the efficiency of an incinerator is, on occasion, due to excessive throughput or choice of operating parameters that are less than desired. For example, the operating temperature inside the plant should be at the specified temperature (usually on the order of 850°C, 1,560°F) to reduce the possible effects of the most dangerous air pollutants and the production of dioxins. A lower than specified combustion temperature implies incomplete incineration, leaving part of the waste in the ashes and other combustion residues. Furthermore, the exhaust gases may be unnecessarily polluting because of the low combustion temperature and the by-products of such combustion may be sent to an unprotected landfill for disposal.

See also: Anaerobic Digestion, Combustion, Biodiesel, Digester, Flue Gas Cleaning, Gasification, Incineration, Waste.

Fuels from Wood

Energy from wood can come in several forms. There are three options currently available for producing heat from wood in the form of (i) logs, (ii) woodchips, and (iii) reconstituted fuels such as pellets and briquettes. Other options which are at the research stage include liquid fuels produced from wood and bales of compressed forest residues.

Logs and wood chips can come from forest thinnings, coppicing, tree-surgery, and pruning operations – even whole trees can be chipped to provide fuel. Woodchips can also be produced from fast-growing varieties of willow and poplar which are cultivated by Short Rotation Coppicing specifically to produce energy. On the other hand, wood pellets are made from highly compressed dry wood shavings and sawdust, usually from sawmilling and joinery operations.

Logs and wood chips can come from forest thinnings, coppicing, tree-surgery, and pruning operations – even whole trees can be chipped to provide fuel. Woodchips can also be produced from fast-growing varieties of willow and poplar which are cultivated by Short Rotation Coppicing specifically to produce energy. On the other hand,

wood pellets are made from highly compressed dry wood shavings and sawdust, usually from sawmilling and joinery operations.

The main processes for the conversion of wood to fuel are, after drying and resizing in which the wood is cut and split in sizes that are easy to transport or before being burned or used as raw material in one of the following processes: (i) carbonization, which is the process of burning wood or biomass in the absence of air breaks it down into liquids, gases, and charcoal, (ii) gasification, which is the process in which solid biomass fuels (e.g., wood, charcoal) are broken down by the use of heat to produce a combustible gas, known as producer gas, (iii) densification, which is used to overcome the bulky nature, low thermal efficiency, and smoke emission of wood and agriculture residues; these can be processed to produce smokeless briquettes with or without binders, (iv) liquid fuel production: for example, ethanol production by alcohol by hydrolysis or anaerobic digestion; liquid fuels can be produced from several biomass types such as wood pulp residues (black liquor), sugarcane, and cassava, and (v) combustion, since biomass fuels can also be used for power generation and/or heat production by direct combustion, either in its primary form or after one or more of the above-mentioned transformation processes.

Generally, biomass fuels such as wood are consumed by direct combustion in their primary form after drying and resizing, or in the form of charcoal. New conversion technologies such as gasification and anaerobic digestion have been developed to provide renewable fuels and to match biomass resources with modern end-use devices. However, as of yet, these technologies are not widely used, so also in the near future, wood energy conversion will consist mainly of resizing, drying, and charcoal production. Nevertheless, in recent years, there has been increasing use of wood and other biomass for energy conversion in modern applications, such as combined heat and power generation (CHP) and co-generation.

Wood fuels consist of three main commodities: fuel wood, charcoal, and black liquor. Fuel wood and charcoal are traditional forest products derived from the forest, trees outside forests, wood processing industries, and recycled wooden products from society. Black liquors are by-products of the pulp and paper industry.

Wood can be used to make both liquid and gaseous fuels. When wood is heated in the absence of air, or with a reduced air supply, it is possible to produce a liquid fuel which can be used in a similar way to conventional oil fuels. It can be used to run internal combustion engines in vehicles or generators. The gas produced from wood is a mixture of hydrogen and carbon monoxide which is similar to the coal gas which was made before the arrival of natural gas from the North Sea. This wood gas can be used in internal combustion engines or in gas turbines which can be used to power generators. Although the liquid fuels are rarely produced from wood at present, wood gas is important in other countries for producing electricity in more remote areas.

Gasification technology is an attractive route for the production of fuel gases from biomass. By gasification, solid biomass is converted into a combustible gas mixture normally called producer gas consisting primarily of hydrogen (H_2) and carbon monoxide (CO), with lesser amounts of carbon dioxide (CO_2), water (H_2O), methane (CH_4), and higher hydrocarbon derivatives (C_xH_y), as well as nitrogen (N_2) and particulates.

The gasification is carried out at elevated temperatures, 500°C and 1,500°C (930 to 2730°F) and at atmospheric or elevated pressures. The process involves conversion of biomass, which is carried out in absence of air or with less air than the stoichiometric requirement of air for complete combustion. Partial combustion produces carbon monoxide as well as hydrogen which are both combustible gases. Solid biomass fuels, which are usually inconvenient and have low efficiency of utilization, can be converted into gaseous fuel. The energy in producer gas is 70% to 80% of the energy originally stored in the biomass. The producer gas can serve in different ways: it can be burned directly to produce heat or used as a fuel for gas engines and gas turbines to generate electricity; in addition, it can also be used as a feedstock for the production of synthesis gas in the production of chemicals, e.g., methanol.

See also: Charcoal, Gaseous Fuels From Wood, Liquid Fuels From Wood, Solid Fuels From Wood, Wood.

Fuel Wood

Fuel wood (fuelwood, firewood) is wood used for conversion to some form of energy, primarily for residential use. Fuel wood usually relates to timber or trees unsuitable for building or construction. Firewood is a renewable resource provided the consumption rate is controlled to sustainable levels. The shortage of suitable firewood in some places has seen local populations damaging huge tracts of bush, thus leading to further desertification.

Fuel wood (i.e., wood itself) is the most common solid fuel and continues to be widely used as a major source of energy for households, especially in developing countries. Charcoal is also increasingly used in many African countries by urban dwellers, as a result of a relentless process of migration of people from rural areas toward urban centers. The major energy end-use in households is cooking, and approximately 86% of fuel wood consumed in urban households in India is for this purpose, while the rest is mostly used for water heating. In Africa, more than 86% of total wood fuels consumption was attributed to the household sector in 1994. Dependence on wood fuels to meet household energy needs is especially high in most of sub-Saharan Africa, where 90 to 98% of residential energy consumption is met from this source.

When used as a solid fuel, some fuel wood (firewood) is harvested in woodlots managed for that purpose, but in heavily wooded areas, it is more usually harvested as a by-product of natural forests. Deadfall that has not started to rot is preferred, since it is already partly seasoned. Standing dead timber is considered better still, as it is both seasoned, and has less rot. Harvesting this form of timber reduces the speed and intensity of bush fires. Harvesting timber for firewood is normally carried out by hand with chainsaws. Thus, longer pieces – requiring less manual labor and less chainsaw fuel – are less expensive (but the user must ensure that the lengths will fit in the firebox!) Prices also vary considerably with the distance from wood lots, and quality of the wood.

In places with high fuel wood and charcoal consumption (due to high population density with low income and/or severe climatic conditions) and weak supply sources, strong pressures are put on existing tree resources, and deforestation and devegetation problems remain a matter of great concern. In addition, urbanization and economic development are bringing changes to the consumption patterns in developing countries, which in turn are leading to major changes in the household energy sector.

In developed countries, heat production by households also remains the major use of fuel wood. For instance, in the European Union, wood fuels account for around 60% of the total wood energy consumed, although their utilization as an industrial energy source for electricity and heat generation is increasing, as a result of new energy policies enacted in most countries to comply with climate change mitigation programs.

See also: Wood.

Fuel Wood – Selection and Preparation

As with any fire, burning wood fuel creates numerous by-products, some of which may be useful (heat and steam), and others that are undesirable, irritating, or dangerous. However, before fuel wood is used, there are several processes that are necessary for application:

Firewood can be sold by weight. Freshly cut (green) wood can contain from 40 to 60% moisture by weight, whereas properly seasoned wood contains only 15 to 20%. Select the driest wood when buying by weight. Green wood will shrink approximately 8% in volume when properly seasoned.

Wood should be dried as much as possible before burning. Properly seasoned wood has approximately 7,700 Btu per pound maximum usable energy per pound versus only approximately 5,000 Btu per pound available from green wood. Wood must be properly stacked for satisfactory drying. The greater the surface area exposed to air, the more rapid the drying. Therefore, stack wood loosely and keep it off moist ground. The stack should be located in an open area for good air circulation – avoid stacking in wood lots for seasoning.

See also: Wood.

Fuel Wood – Use

Cellulose and hemicelluloses form mainly volatile products on heating due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular weight fragments. The progressive increase in the pyrolysis temperature of the wood led to the release of the volatiles, thus forming a solid residue that is different chemically from the original starting material. Cellulose and hemicelluloses initially break into

compounds of lower molecular weight. This forms activated cellulose which decomposes by two competitive reactions: one forming volatiles (anhydrosugars) and the other char and gases. The thermal degradation of the activated cellulose and hemicelluloses to form volatiles and char can be divided into categories depending on the reaction temperature. Within a fire, all these reactions take place concurrently and consecutively. Gaseous emissions are predominantly a product of pyrolytic cracking of the fuel. If flames are present, fire temperatures are high, and more oxygen is available from thermally induced convection.

See also: Charcoal, Wood.

Functional Group

One of the issues that arise when dealing with alternative fuels from biomass (e.g., bio-oil) is the presence of functional groups in the organic product(s). The presence of functional group not only affects the properties of the bio-oil but also affects the selection of the appropriate process required for the conversion of the bio-oil to useful products such as fuels.

A functional group is the part of an organic molecule which contains atoms other than carbon and hydrogen, or which contain bonds other than a carbon-carbon single bond (C-C) and a carbon-hydrogen bond (C-H). Some of the most common functional groups in organic chemistry are alkenes, alkynes, aromatics, nitriles, amines, amides, nitro compounds, alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids, acid chlorides, acid anhydrides, esters, alkyl halides, thiols, and thioethers.

Functional groups are attached to the carbon backbone of organic molecules. They determine the characteristics and chemical reactivity of molecules. Functional groups are far less stable than the carbon backbone and are likely to participate in chemical reactions. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule. However, its relative reactivity can be modified by nearby functional groups.

The non-hydrogen atoms of functional groups are always associated with each other and with the rest of the molecule by covalent bonds. When the group of atoms is associated with the rest of the molecule primarily by ionic forces, the group is referred to more properly as a polyatomic ion or complex ion.

Compounds that contain carbon-oxygen single bonds (C-O bonds) each possess differing reactivity based upon the location and hybridization of the carbon-oxygen single bond, owing to the electron-withdrawing effect of sp^2 hybridized oxygen and the donating effects of sp^3 hybridized oxygen. Compounds that contain nitrogen in this category may contain C-O bonds, such as in the case of amides.

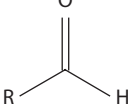
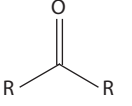
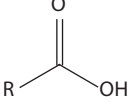
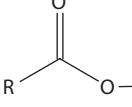
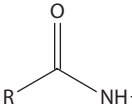
Thus, a functional group is any atom or collection of atoms that is capable of reacting with a reactive species to produce a product and is also capable of affecting the properties of the original non-functional molecule in which the group occurs. Some of the most common functional groups in organic chemicals are (i) the double bond of alkene derivatives, $R_1C=CR_2$, (ii) the triple bond of alkyne derivatives, $R_1C\equiv CR_2$, (iii) the aromatic ring in aromatic derivatives such as in benzene derivatives and including the ring systems in condensed-ring aromatic derivative, (iv) the carbon-nitrogen function in nitrile derivatives, $RC\equiv N$, (v) the carbon-nitrogen function in amine derivatives RNH_2 , R_1NHR_2 , and $R_1NH(R_3)R_2$, (vi) the oxygen-carbon-nitrogen function in amide derivatives ($RC(=O)NH_2$), (vii) the nitrogen-oxygen function in nitro compounds, RNO_2 , (viii) the oxygen-hydrogen function in alcohol derivatives, ROH , (ix) the oxygen-hydrogen function in phenol derivatives, $ArOH$, (x) the carbon-oxygen-carbon function in ether derivatives, R_1OR_2 , (xi) the carbon-oxygen double bond in aldehyde derivatives, $RCH=O$, (xii) the carbon-oxygen double bond in ketone derivatives, R_1COR_2 , (xiii) the carbon-oxygen double bond and oxygen-hydrogen bond in carboxylic acid derivatives, RCO_2H , (xiv) the carbon-oxygen double bond and oxygen-chloride bond in acid chloride derivatives, $RCOCl$, (xv) the carbon-oxygen-carbon bond in acid anhydride derivatives, $R_1CO-O-COR_2$, (xvi) the carbon-oxygen-carbon bond in ester derivatives, R_1COOR_2 , (xvii) the carbon-halogen bond in alkyl halide derivatives, RX , where X is a halogen, (xviii) the sulfur-hydrogen bond in thiol derivatives, RSH , and (xix) the carbon-sulfur-carbon bond in thioether derivatives R_1SR_2 . In each of the aforementioned examples, R_1 and R_2 are alkyl groups (the same or different) and Ar is a phenyl group or other aromatic group.

Table F-1 General properties of functional group compounds.

Group	Polarity	Volatility/melting point/boiling point	Soluble in water	Acid-base behavior	Common compounds
Alkanes C_nH_{2n+2}	Non-polar	Very volatile, smaller molecules are gases Boiling point increases with size due to increased dispersion forces and larger mass	No	None	Methane, propane, butane, octane, and higher molecular weight hydrocarbons, including wax
Alkenes/Alkynes C_nH_{2n}/C_nH_{2n-2}	Non-polar	Have similar b.p. to alkanes w/ same # of carbons but a few degrees lower since they have fewer electrons = less dispersion forces	No	None	
Halo-alkanes RX	Slightly Polar – non-polar	Most halo-alkanes are liquids at room temperature Only CH_3Cl , CH_3Br and CH_3CH_2Cl are gasses Dispersion forces are more important than dipole-dipole forces B.P. decreases with # of substituents since temporary dipole is stronger for long chains and attractions are more effective when molecules can pack closely	Slightly	None	Polyvinyl chloride Chlorofluorocarbons Teflon
Alcohols ROH	Polar bond capable of H-bonds	Volatile when pure but often mixed w/ H_2O Higher boiling points than alkanes b/c of hydrogen bonding Volatility and B.P. increase as length of chain increases	Yes, decreases w/ length of carbon chain	Weakly acidic and basic (amphoteric) like water b/c of $-OH$	Ethanol, isopropyl alcohol, menthol
Ethers ROR	Polar bonds, no H-bonds	Volatile Lower boiling points than alcohols b/c no hydrogen bonding			First anesthetic – diethyl ether
Amines RNH_2 or R_2NH or R_3N	Polar bonds, capable of H-bonds	Low volatility High boiling points b/c of H-bonding	Yes	Basic b/c of lone pair, $R-NH_2$ even more basic than NH_3	Amino acids Ammonia

(Continued)

Table F-1 General properties of functional group compounds. (*Continued*)

Group	Polarity	Volatility/melting point/boiling point	Soluble in water	Acid-base behavior	Common compounds
Aldehydes RCHO 	Polar carbonyl group (C=O) H-bond can form between carbonyl and water	B.P. is higher than that of similarly sized alkanes b/c of dipole-dipole forces. B.P. is lower than alcohols since dipole-dipole forces are weaker than H-bonds. B.P. increase with size of carbon chain	Yes, decreases w/ length of carbon chain	Carbonyl can act as a base	Formaldehyde
Ketones RCOR 	Polar carbonyl group (C=O) H-bond can form between carbonyl and water	See aldehydes	Yes, decreases w/ length of carbon chain	Carbonyl can act as a base	Acetone (nail polish remover)
Carboxylic Acids RCOOH 	Polar, capable of hydrogen bonds	Low volatility Higher boiling points b/c of hydrogen bonding	Yes decreases w/ length of carbon chain	Acid Methanoic is stronger than ethanoic b/c of R group.	Acetic acid – vinegar
Esters RCOOR 	Polar, no H-bonds H-bond can form between carbonyl and water	More volatility than carboxylic acids and lower boiling points b/c can't H-bond Liquids at room temp for smaller molecules	Small esters: yes, solubility decreases w/ size of chain		Polyesters Fatty acids
Amides 	Polar, amine can hydrogen bond	High m.p. b/c of hydrogen bonding Amides are liquids or solids at room temp	Yes	Amine part of amide is basic	Proteins Polypeptides Nylon

Fungi

A fungus (plural: fungi) is any member of the group of eukaryotic organisms that includes microorganisms such as yeasts and molds, as well as the more familiar mushrooms.

Fungi are non-photosynthetic organisms and frequently possess a filamentous structure. Some fungi are as simple as the microscopic unicellular yeasts, whereas other fungi form large, intricate toadstools. The microscopic filamentous structures of fungi generally are much larger than bacteria and usually are 5-10 microns in width. Fungi are aerobic (oxygen-requiring) organisms and generally can thrive in more acidic media than can bacteria. They are also more tolerant of higher concentrations of heavy metal ions than are bacteria.

Perhaps the most important function of fungi in the environment is the breakdown of cellulose in wood and other plant materials. To accomplish this, fungal cells secrete a biological catalyst (enzyme) called cellulase. This enzyme

breaks insoluble cellulose down to soluble carbohydrates that can be absorbed by the fungal cell. Because it acts outside the organism, it is called an extracellular enzyme or exoenzyme.

Although fungi do not grow well in water, they play an important role in determining the composition of natural waters and wastewaters because of the large amount of their decomposition products that enter water. An example of such a product is humic material, which interacts with hydrogen ions and metals.

Fusion Energy

Fusion is a form of nuclear energy that can be used to produce electricity in large base load power plants. The basic nuclear processes involved occur at the opposite end of the spectrum of atomic masses than fission. Specifically, fission involves the splitting of heavy nuclei such as uranium-235 (^{235}U). Fusion involves the merging (i.e., the fusing) of light elements, mainly hydrogen (H , ^1H) and the hydrogen isotopes deuterium (D , ^2H) and tritium (T , ^3H).

There are three main advantages of fusion power: (i) fuel reserves, (ii) environmental impact, and (iii) safety.

In terms of the fuel reserves, there are two main reactions of interest that occur at a fast enough rate to produce electricity. These involve pure deuterium and an equal mix of deuterium and tritium. Deuterium occurs naturally in ocean water. There is 1 atom of deuterium for every 6,700 atoms of hydrogen, and deuterium can be easily extracted at a low cost. If all the deuterium in the ocean were used to power fusion reactors utilizing a standard steam cycle, there would be enough energy generated to power the earth for approximately 2 billion years (2×10^9 years) at the present rate of total world energy consumption.

The deuterium–tritium (D-T , $^2\text{H-}^3\text{H}$) reaction produces more energy than a pure deuterium (D-D , $^2\text{H-}^2\text{H}$) reaction. However, the main advantage is that deuterium–tritium reactions occur at a faster rate, thereby making it easier to build such a reactor. Consequently, all first generation fusion reactors will use deuterium–tritium. In terms of reserves, the multi-billion years of deuterium applies to deuterium–tritium as well as deuterium–deuterium reactors. However, since tritium is a radioactive isotope with a half-life on the order of 12 years, there is no natural tritium to be found on earth. Instead, tritium is obtained by breeding with the lithium isotope lithium-6 (^6Li) which is one of the components in the fusion blanket.

The next advantage is the environmental impact of fusion. Fusion reactions produce no carbon dioxide or other greenhouse emissions. Fusion reactions also do not emit any other harmful chemicals into the atmosphere. The main end product of the fusion reaction is the harmless, inert gas helium (He). The biggest environmental issue in fusion is that one by-product of both the deuterium–deuterium and the deuterium–tritium reaction is a high-energy neutron. These neutrons are captured in the fusion blanket so they pose no threat to the public. However, as they pass through structural material on their way to the blanket, the neutrons cause the structure to become activated. Even so, this radioactive structural material has a short half-life so that the storage time required once it is removed is also short, on the order of 100 years. Overall, the entire environmental situation, fusion, is an attractive option.

The last major advantage involves safety. Here, since fusion is a nuclear process, there is concern related to the possibility of a radioactive meltdown. The basic laws of physics governing fusion reactions make this an unlikely (if not impossible) event. Specifically, in a fission reactor, the entire energy content corresponding to several years of power production is stored within the reactor core at any instant of time. It is this huge energy content that makes a meltdown possible. A fusion reactor does not depend on maintaining a chain reaction in a large sitting mass of fuel. Instead, fuel must be constantly fed into the reactor at a rate allowing it to be consumed as needed. The end result is that at any instant of time, the mass of fuel in a fusion reactor is small, perhaps corresponding to the weight of several postage stamps. It is this small instantaneous mass of fuel that makes a meltdown impossible in a fusion reactor.

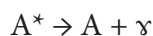
See also: Nuclear Energy, Nuclear Fission, Nuclear Fusion.

Gamma Decay

Gamma decay (γ -decay) is a type of radioactive decay that an excited nucleus (A^*) can undergo. In contrast to alpha decay and beta decay, no particles are ejected from the nucleus when it undergoes this type of decay, but, instead, a high energy form of electromagnetic radiation – a gamma ray photon (γ) – is released leaving an unexcited nucleus (A).

Gamma rays are simply photons that have extremely high energies which are highly ionizing. Gamma radiation is unique in the sense that undergoing gamma decay does not change the structure or composition of the atom but does change the energy of the atom since the gamma ray carries no charge nor does it have an associated mass. In order for a nucleus to undergo gamma decay, it must be in some sort of excited energetic state.

Protons and neutrons are located in discrete energy states within the nucleus, not too different from the excited states that the electrons can occupy in atoms. If a proton or a neutron in nucleus is converted to an excited state – typically after alpha decay or beta decay – the new daughter nucleus must somehow release energy to allow the proton or neutron to relax back down to ground state. When the nucleon makes this transition from a high to a low energy state, a gamma photon is emitted. The general equation that represents this process is:



In this equation, A^* is the excited atom, A is a relaxed state of the initial excited atom, and γ is the released gamma ray photon.

The number of protons and neutrons in the nucleus does not change in this process, so the parent and daughter atoms are the same chemical element. In the gamma decay of a nucleus, the emitted photon and recoiling nucleus each have a well-defined energy after the decay. The characteristic energy is divided between only two particles.

Both uranium-238 (^{238}U) and uranium-235 (^{235}U) that are used as fuel for nuclear power plants undergo both alpha and gamma decays when used. Immediately following the fission process, gamma rays are released, resulting in high levels of radiation present around the reactor.

See also: Alpha Decay, Beta Decay, Nuclear Energy, Nuclear Fission.

Gas Analysis

The only special features characterizing the sampling of gas stream the potential for the separation of liquid phase material when the ambient conditions change, and this effect can be reversed by restoring the original conditions.

Despite the great value of analytical procedures, however, many empirical tests relating to chemical and physical characteristics are carried out, either because they are more convenient, or more accurate, than determinations dependent upon analysis. Currently, the preferred method for the analysis of a gas stream is gas chromatography (for example, ASTM D2163) which will allow identification and measurement of the main components and traces, but it should be noted that gas chromatography is not entirely satisfactory for determining traces of higher boiling hydrocarbon derivatives.

Mass spectrometry (ASTM D2650) is also suitable for analysis of crude oil gases, but is not likely to be used if the chromatographic apparatus is already available. Of the other spectroscopic techniques, infrared and ultra-violet absorption may be applied to gas analysis for some specialized applications. Gas chromatography has also largely supplanted chemical absorption methods of analysis, but again these may have some limited specialized application.

Satisfactory combustion of hydrocarbon gases depends upon the matching of burner and appliance design with certain gas characteristics. The most important of these are the Wobbe index [calorific value/(specific gravity)], and the flame speed, usually expressed as a factor or an arbitrary scale on which that of hydrogen is 100.

The Wobbe index – originally developed for natural gas but applicable to other gas streams – gives a measure of the heat input to an appliance through a given aperture at a given gas pressure. Using this as a vertical coordinate and the flame speed factor as the horizontal coordinate, a combustion diagram can be constructed for an appliance, or a whole range of appliances, with the aid of appropriate test gases. This diagram shows the area within which variations in the Wobbe index and of gases may occur for the given range of appliances without resulting in incomplete combustion or flame lift or the lighting back of pre-aerated flames. This method of prediction of combustion characteristics is not sufficiently accurate to eliminate entirely the need for the practical testing of new gases.

The carbon/hydrogen ratio is of importance since it is normally uneconomical to recover the latent heat of the water vapor resulting from combustion. This results in higher heat losses in waste gas from the combustion of gaseous hydrocarbon derivatives than from other fuels. This effect largely counteracts the higher combustion efficiency which would otherwise be obtainable from the use of hydrocarbon gases owing to their superior flexibility and controllability.

Analytical methods are available in standard form for determining volatile sulfur content and certain specific corrosive sulfur compounds that are likely to be present. Many laboratories use rapid combustion techniques with an oxy-hydrogen flame (ASTM D2784). Absorption methods are suitable for determination of particular sulfur compounds, while other procedures have been developed in which the sulfur compounds are titrated electrometrically after absorption in alkaline solutions.

Trace hydrocarbon derivatives that may be regarded as contaminants may be determined by the gas chromatographic methods already discussed. Heavier hydrocarbon derivatives in small amounts may not be completely removed from the column. If accurate information is required related to the nature and amount of high-boiling constituents, then temperature programming or a reconcentration procedure may be used.

The quantitative determination of water content is carried out by titration with Karl Fischer reagent, and analytical methods for determining traces of various other impurities are known to be in use. No published methods are available, but procedures based on standard analytical practice have been worked out for traces of ammonia, alkali, and alkali metals. The method for determination of inert gases in a gas stream based on absorption of the hydrocarbon derivatives in glacial acetic acid using an Orsat-type apparatus has been superseded by gas chromatography.

Once the composition of a mixture has been determined, it is possible to calculate various properties. Values which can be derived in this way include specific gravity, vapor pressure, calorific value, and dew point. Where it is necessary therefore to carry out the full analysis for some purpose, or where the facilities (gas chromatography) are available to do it, empirical tests may not be necessary.

One of the most widely used tests is vapor pressure (ASTM D126) which set out instructions for the test at 100°F (38°C). Simple evaporation tests in conjunction with vapor pressure measurement give a further guide to composition. In these tests, a gas stream is allowed to evaporate naturally from an open graduated vessel. Results are recorded on the basis of volume/temperature changes, such as the temperature recorded when 95% has evaporated, or volume left at a particular temperature. In one form of the test, the temperature is taken as the freezing point of mercury. The results are interpreted in relation to commercial butane or butane-propane mixtures.

Since dew point can be calculated from composition, direct determination of dew point for a particular gas stream type is a measure of composition. It is of more direct practical value, and if there are small quantities of higher molecular weight material present, it is preferable to use a direct measurement. The method is essentially a simple one of basic physics, but skill and experience are necessary to detect the haze formation correctly and to distinguish between the required hydrocarbon dew point and a film due to moisture. Equipment is available for both manual measurement and automatic recording of the dew point.

Specific gravity of the gas stream can be calculated, but if it is necessary to measure it, several pieces of apparatus are available; the determination can be carried out using a metal pressure pycnometer. Various procedures, manual, and recording, for specific gravity or density in the gaseous state are given in ASTM D1 070. Various types of calorimeter are available for the direct determination of calorific value. Suitable equipment is described in standard test methods ASTM D900 and ASTM D1826.

Corrosive sulfur compounds can be detected by their effect on copper and the form in which the general copper strip corrosion test and hydrogen sulfide can be detected by its action on moist lead acetate paper, and a procedure is also used as a measure of sulfur compounds.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Gas Cleaning

Gas cleaning (gas processing, gas refining) usually involves the use of several integrated unit processes to remove: (i) water, (ii) elements such as sulfur, helium, and carbon dioxide, and (iii) higher-boiling hydrocarbon derivatives, often referred to as gas liquids. In addition, it is often necessary to install scrubbers and heaters at or near the well-head that serve primarily to remove sand and other large-particle impurities. The heaters ensure that the temperature of the gas stream does not drop too low and form a hydrate with the water vapor content of the gas stream.

Gas cleaning, which involves a variety of methods (Table G-1), is a necessary step in many process industries in order to control the particulate matter emission and maintain a high level of environmental protection.

Table G-1 Summary of processes used for gas cleaning.

Separation concept	Process	Principle
Adsorption	Pressure Swing adsorption	Adsorption of CO ₂ using a molecular sieve
Physical absorption	Pressurized water wash	Dissolution of CO ₂
	Selexol, Rectisol, Purisol processes	Dissolution of CO ₂ in a specialized solvent
Chemical absorption	Alkanolamine wash	Chemical reaction of CO ₂ with the alkanolamine
Membrane separation	Polymer membrane (dry separation)	Membrane permeability of H ₂ S and CO ₂ is higher than CH ₄
Cryogenic process	Low temperature process	Phase transformation of CO ₂ to liquid; CH ₄ remains gaseous

Furthermore, in terms of their use as fuels or as feedstocks for the production fuels, gaseous products are experiencing a period of rapid development and, as a result, gas upgrading is attracting increasing attention. Currently, many of the gaseous products are used as on-site (refinery) fuel in power generators and boilers, and, for these uses, the hydrogen sulfide content in the gas should be less than 200 parts per million (ppm v/v) to ensure a long life for the power and heat generators. Consequently, the market for clean gas that is free of pollutants is facing significant challenges in terms of energy consumption and operating costs.

Many chemical processes are available for cleaning gas streams. However, there are many variables in the choice of process of the choice of refining sequence that dictate the choice of process or processes to be employed. In this choice, several factors must be considered: (i) the types and concentrations of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide and carbon dioxide, gas may contain other contaminants, such as mercaptans (also called *thiols*, R-SH) and carbonyl sulfide (COS). In fact, the variation in the composition of the gases that require cleaning either before being assigned to further use requires a variation of process types to ensure that specifications are met and the environment is protected. The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes also capable of removing the acid gas impurities to very low levels when the acid gases are there in low-to-medium concentrations in the gas.

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

The most common technologies utilized are venturi-type scrubbers, disintegrators, bag filters, and electrostatic precipitators. However, the selection of a cleaning technology (or technologies) is site-specific, case-sensitive, and dependent on the gas utilization requirements and local circumstances. However, it is important to recognize the composition of the gas so that the appropriate technologies can be selected for use to remove the specific contaminants. Thus, when any biomass-derived gas (either synthesis gas or bio-synthesis gas) is used for biofuel production, the cleaning of the raw gas is needed strictly in order to remove contaminants and potential catalyst poisons as well as to achieve the qualitative composition required before the gas is sold for use.

A gas stream gas, as produced by any methods such as anaerobic digestion, pyrolysis, or gasification, is typically saturated with water vapor and contains, in addition to methane (CH_4) and carbon dioxide (CO_2), various amounts of hydrogen sulfide (H_2S) as well as other contaminants that vary in amounts depending upon the composition of the feedstock and the process parameters employed for production of the gas. The properties of the contaminants are such that failure to remove them will make the gas unusable and even poisonous to the user. For example, hydrogen sulfide is a toxic gas, with a specific, unpleasant odor, similar to rotten eggs, forming acidic products in combination with the water vapor in the gas stream which can also result in corrosion of equipment. To prevent this, and a similar example of the adverse effects of other contaminants, the gas stream must be dried and any contaminants removed before the gas stream is sent to one or more conversion units or for sales.

Typically, in the gas cleaning industry (also called the *gas processing industry* or the *gas refining industry*), the feedstock is not used directly as fuel because of the complex nature of the feedstock and the presence of one or more of the aforementioned impurities that are corrosive or poisonous. It is, therefore, essential that any gas should be contaminant free when it enters any one of the various reactors. Typically, the primary raw gas stream has been subjected to chemical and/or physical changes (refining) after being produced. Thus, for many applications, the quality of the gas stream has to be improved. In addition, landfill gas often contains significant amounts of halogenated compounds which need to be removed prior to use. Occasionally, the oxygen content is high when air is allowed to invade the gas producer during collection of the landfill gas or when the biomass from which the gas is produced contains an abundance of oxygen-containing organic constituents.

The main contaminants (but not necessarily the only contaminants) that may require removal in gas cleaning systems are hydrogen sulfide, water, carbon dioxide, and halogenated compounds. Desulfurization prevents corrosion and avoids concentrations of the toxic hydrogen sulfide for safety in use and in the workplace. Also, if hydrogen sulfide and other sulfur-containing species such as thiol derivatives (RSH , also called mercaptan derivative) and carbonyl sulfide (COS) are not removed, combustion of the gas produces sulfur dioxide and sulfur trioxide which is even more poisonous than hydrogen sulfide. At the same time, the presence of sulfur dioxide in the gas stream lowers the dew point (the temperature to which the gas must be cooled to become saturated with water vapor) in the stack gas. The sulfurous acid formed (H_2SO_3) by reaction of the sulfur dioxide and the water vapor as well as the reaction of carbon dioxide and the water vapor form highly corrosive acidic species:



Thus, the removal of water from the gas stream is also essential, not only because of the potential for the reaction of water with contaminants in the gas stream but also because of potential accumulation of water vapor condensing in the gas line, the formation of a corrosive acidic solution when hydrogen sulfide is dissolved, or to achieve low dew points when the gas stream is stored under elevated pressures in order to avoid condensation and freezing. Also, if the non-combustible carbon dioxide is not removed, the energy content of the gas stream is diluted and there may also be an environmental impact due to the presence and emission of this contaminant.

Generally, the contaminants – not on any order of importance – are categorized as (i) condensable hydrocarbon derivatives, including tar products, (ii) alkali metals, such as sodium and potassium, (iii) nitrogen-containing derivatives, including ammonia and hydrogen cyanide, (iv) sulfur-containing derivatives, such as hydrogen sulfide, carbonyl sulfide, and carbon disulfide, (v) halogen-containing derivatives, such as hydrogen chloride and hydrogen bromide, and hydrogen fluoride, and (vi) particulate matter.

The constituents that make up the tar-like products that are formed during gasification when biomass decomposes in pyrolysis and gasification reactions are mostly oxygenated compounds that are decomposition products of biomass. These compounds react further and form secondary and tertiary tar compounds, which consist of compounds that do not exist in the source biomass. The secondary tar typically consists of alkylated one-ring and two-ring aromatic compounds (including heterocyclic compounds), whereas tertiary tar consists of aromatic hydrocarbon derivatives such as benzene, naphthalene, and various polycyclic aromatic hydrocarbon derivatives (PAHs, also called polynuclear aromatic compounds, PNAs). Tar constituents are typically classified on the basis of the number of rings (or the size of the condensed-ring systems) in the constituents or by boiling point distribution or physical properties. More generally, tar is defined as aromatic compounds that are higher-boiling than benzene and, in addition, an operational definition for tar depending on the end-use application has been used.

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

See also: Gas Processing, Gas Treating.

Gas Cleaning – Alkali Washing Processes

Alkali washing processes typically fall under the general banner of *scrubber-based processes* (e.g., chemical scrubbers, gas scrubbers) which are a diverse group of gas cleaning processes that can be used to remove some particulate matter and/or gases from industrial exhaust streams (Figure 8.8). Traditionally, the term *scrubber* is used to refer to devices that use a liquid to wash and remove contaminants from gas streams. More recently, the term has also been used to describe systems that inject a dry reagent or a slurry into a contaminated gas stream to wash out acid gases.

The process efficiency for the removal of contaminants is improved by increasing the residence time of the gas stream in the scrubber or by increasing the surface area of the scrubber solution by the use of a spray nozzle or a packed tower. A wet scrubbing system has the potential to increase the proportion of water in the treated gas stream.

Wet scrubbers can also be used for heat recovery from hot gases by flue-gas condensation. In this option, water from the scrubber drain is circulated through a cooler to the nozzles at the top of the scrubber. The hot gas enters the scrubber at the bottom, and, if the gas temperature is above the dew point of the water, it is initially cooled by evaporation of the water drops. Further cooling causes water vapor to condense thereby adding to the amount of circulating water.

See also: Alkali Washing Process.

Gas Cleaning – Biological Methods

Biological processes have mainly been used to remove hydrogen sulfide. Hydrogen sulfide can be oxidized by microorganisms of the species *Thiobacillus* and *Sulfolobus*. The degradation requires oxygen, and therefore, a small amount of air (or pure oxygen if levels of nitrogen should be minimized) is added for biological desulfurization to take place. The degradation can occur inside the digester and can be facilitated by immobilizing the microorganisms occurring naturally in the digestate. An alternative is to use a trickling filter which the gas stream passes through when leaving the digester. In the trickling filter, the microorganisms grow on a packing material. A gas stream with added air meets a counterflow of water containing nutrients. The sulfur-containing solution is removed and replaced when the pH drops below a certain level. Both methods are widely applied; however, they are not suitable when the gas stream

is used as vehicle fuel or for grid injection due to the remaining traces of oxygen. An alternative system is available in which the absorption of the hydrogen sulfide is separated from the biological oxidation to sulfur – hence, the gas stream flow remains free of oxygen. There has also been focus on the removal of siloxane derivatives and carbon dioxide.

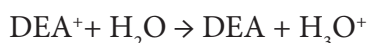
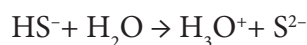
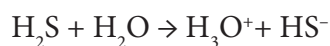
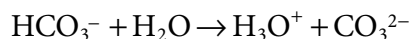
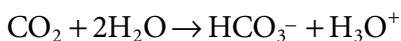
As another example, natural bacteria can convert hydrogen sulfide into elemental sulfur in the presence of oxygen and iron. This can be done by introducing a small amount (2 to 5%) of air into the head space of the digester. As a result, deposits of elemental sulfur will be formed in the digester. Even though this situation will reduce the hydrogen level, it will not lower it below that recommended for pipeline-quality gas. This process may be optimized by a more sophisticated design where air is bubbled through the digester feed material. It is critical that the introduction of the air be carefully controlled to avoid reducing the amount of the gas stream that is produced.

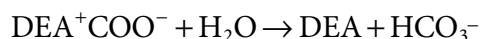
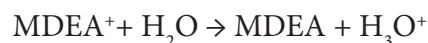
See also: Biofiltration, Bio-oxidation, Bioscrubbing.

Gas Cleaning – Chemisorption

Chemisorption (chemical absorption) processes are characterized by a high capability of absorbing large amounts of acid gases. They use a solution of a relatively weak base, such as monoethanolamine. The acid gas forms a weak bond with the base which can be regenerated easily. Monoethanolamine and diethanolamine derivatives are frequently used for this purpose. The amine concentration typically ranges between 15 and 30% w/w. The gas stream is passed through the amine solution where sulfides, carbonates, and bicarbonates are formed. Diethanolamine is a favored absorbent due to its lower corrosion rate, smaller amine loss potential, fewer utility requirements, and minimal reclaiming needs. Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS), while the mono- reacts irreversibly with 95% of the carbonyl sulfide and forms a degradation product that must be disposed in an environmentally acceptable manner.

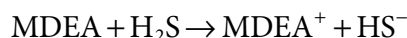
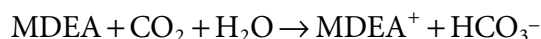
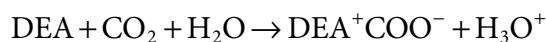
The ethanolamine process, known as the *Girbotol* process, removes acid gases (hydrogen sulfide and carbon dioxide) from gases. The Girbotol process uses an aqueous solution of ethanolamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower (the absorber) through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator. Alkanolamine scrubbers can be used to remove hydrogen sulfide or hydrogen sulfide and carbon dioxide simultaneously. For instance, monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and triethanolamine (TEA) can be used. The alkanolamine scrubbing process is also carried out in two steps: the first step involves the amine contactor, and the second step involves the regenerator. In a process with diethanolamine and methyldiethanolamine, the main reactions in equilibrium in the system are:





The pH is an important parameter because it affects the concentration of the ionic species and therefore the reactions with the amines. Moreover, the temperature and pressure also have a significant effect on the process.

The reactions that involve carbon dioxide and hydrogen sulfide with amines are as follows:



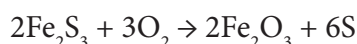
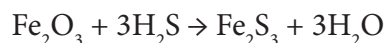
This system is very complex due to the number of reactions involved, and other reactions may also occur in the system. Tertiary amines such as DMEA do not react directly with carbon dioxide, and hydrogen sulfide with amines is almost instantaneous by proton transfer. Thus, tertiary amines are used for selective hydrogen sulfide removal, and for selective hydrogen sulfide and carbon dioxide removal, a mixed amine system (tertiary and primary or secondary) is employed. Moreover, other compounds can be mixed with amine solutions.

Thus, treatment of a gas stream to remove the acid gas constituents (hydrogen sulfide and carbon dioxide) is most often accomplished by contact of the gas stream with an alkaline solution. The most commonly used treating solutions are aqueous solutions of the ethanolamine or alkali carbonates, although a considerable number of other treating agents have been developed in recent years. Most of these newer treating agents rely upon physical absorption and chemical reaction. When only carbon dioxide is to be removed in large quantities or when only partial removal is necessary, a hot carbonate solution or one of the physical solvents is the most economical selection.

The primary process for sweetening sour gas uses an amine (*olamine*) solution to remove the hydrogen sulfide (the *amine process*). The sour gas is run through a tower, which contains the olamine solution. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from the gas stream as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. The amine solution used can be regenerated for reuse and, although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponge to remove hydrogen sulfide and carbon dioxide, including bio-based iron sponge.

Diglycolamine (DGA) is another amine solvent used in the Econamine process in which absorption of acid gases occurs in an absorber containing an aqueous solution of diglycolamine, and the heated rich solution (saturated with acid gases) is pumped to the regenerator (Reddy and Gilmartin, 2008). Diglycolamine solutions are characterized by low freezing points, which make them suitable for use in cold climates.

The most well-known hydrogen sulfide removal process is based on the reaction of hydrogen sulfide with iron oxide (often also called the iron sponge process or the dry box method) in which the gas is passed through a bed of wood chips impregnated with iron oxide. The iron oxide is converted to the corresponding sulfur which is re-aerated by oxidation:

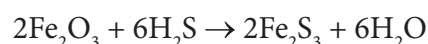


The iron oxide process (which was implemented during the 19th century and also referred to as the iron sponge process) is the oldest and still the most widely used batch process for sweetening the gas stream. The reaction can be exploited by adding the iron chloride to the digester feed material or passing the gas stream through a bed of

iron oxide-containing material. The iron oxide comes in different forms such as rusty steel wool, iron oxide pellets, or wood pellets coated with iron oxide. The iron oxide media needs to be replaced periodically. The regeneration process is highly exothermic and must be controlled to avoid problems.

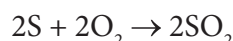
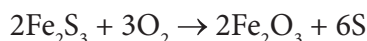
In the process, the sour gas is passed down through the bed. In the case where continuous regeneration is to be utilized, a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the on-stream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove. Ferric hydroxide $[\text{Fe}(\text{OH})_3]$ can also be used in this process.

The process is usually best applied to gases containing low-to-medium concentrations (300 ppm v/v) of hydrogen sulfide or mercaptan derivatives. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is usually high purity. The use of iron oxide process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:



The reaction requires the presence of slightly alkaline water, and a temperature below 43°C (110°F) and bed alkalinity (pH: 8 to 10) should be checked regularly, usually on a daily basis. The pH level is maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the incoming gas stream (i.e., the gas stream at the inlet).

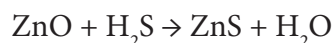
The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:



The regeneration step is exothermic, and air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly, the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles, this sulfur will form a cake over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles, the bed must be removed and a new bed introduced into the vessel.

The iron oxide process is one of several metal oxide-based processes that scavenge hydrogen sulfide and organic sulfur compounds (mercaptan derivatives) from gas streams through reactions with the solid-based chemical adsorbent (Kohl and Riesenfeld, 1985). They are typically non-regenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most of the processes are governed by the reaction of a metal oxide with hydrogen sulfide to form the metal sulfide. For regeneration, the metal oxide is reacted with oxygen to produce elemental sulfur and the regenerated metal oxide. In addition, to iron oxide, the primary metal oxide used for dry sorption processes is zinc oxide.

In the zinc oxide process, the zinc oxide media particles are extruded cylinders 3-4 mm in diameter and 4 to 8 mm in length and react readily with the hydrogen sulfide:

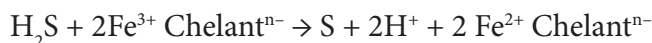


At increased temperatures (205 to 370°C , 400 to 700°F), zinc oxide has a rapid reaction rate, therefore providing a short mass transfer zone, resulting in a short length of unused bed and improved efficiency.

Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the *Ferrox* process or the *Stretford* process. The *Ferrox* process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The *Stretford* process employs a solution containing vanadium salts and anthraquinone disulfonic acid (Maddox, 1974; Mokhatab et al., 2006; Abdel-Aal et al., 2016).

Most hydrogen sulfide removal processes return the hydrogen sulfide unchanged, but if the quantity involved does not justify installation of a sulfur recovery plant (usually a Claus plant), it is necessary to select a process that directly produces elemental sulfur. In the *Beavon-Stretford* process, a hydrotreating reactor converts sulfur dioxide in the off-gas to hydrogen sulfide which is contacted with Stretford solution (a mixture of vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide) in a liquid-gas absorber. The hydrogen sulfide reacts stepwise with sodium carbonate and anthraquinone disulfonic acid to produce elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber.

Even though the removal of hydrogen sulfide can be achieved by chemical or physical absorption, chemical scrubbers are the most commonly used systems for hydrogen sulfide removal. The most important processes are iron-based chelation methods and absorption by alkanolamines. In iron-based chelation processes, there are two main reactions:



The first step involves the chemical reaction to produce elemental sulfur, and in the second step, iron(III) is regenerated. Several commercial processes are based on iron chelation, such as the Lo-cat and Sulferox processes. Ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA) are the most conventional ligands used in this process. The operating conditions are typically: 4 to 8°C (39.5 to 46.5°F), pH 4 to pH 8, iron concentration on the order of 1,000 to 10,000 ppm v/v with a chelant/iron ratio in the range 1.1 to 2.0.

The process using potassium phosphate is known as phosphate desulfurization, and it is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbon derivatives as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally. Processes using ethanolamine and potassium phosphate are now widely used.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Gas Cleaning – Effects of Gas Composition

Trace quantities of contaminants in hydrocarbon products can be harmful to many catalytic chemical processes in which these products are used. In general, the raw product gas of biomass gasification contains a range of minor species and contaminants, including particles, tar, alkali metals, chlorine compounds such as hydrogen chloride (HCl), nitrogen compounds such as ammonia (NH_3) and hydrogen cyanide (HCN), sulfur compounds such as hydrogen sulfide (H_2S) and carbonyl sulfide (COS), as well other species.

The maximum permissible levels of total contaminants are normally included in specifications for such hydrocarbon derivatives. It is recommended that this test method be used to provide a basis for agreement between two laboratories when the determination of sulfur in hydrocarbon gases is important. In the case of liquefied petroleum gas (LPG), total volatile sulfur is measured on an injected gas sample.

Acidic constituents such as carbon dioxide and hydrogen sulfide as well as thiol derivatives (RSH, also called mercaptan derivatives) can contribute to corrosion of refining equipment, harm catalysts, pollute the atmosphere, and prevent the use of hydrocarbon components in petrochemical manufacture. When the amount of hydrogen sulfide is high, it may be removed from a gas stream and converted to sulfur or sulfuric acid; a recent option for hydrogen sulfide removal is the use of chemical scavengers. Some gases contain sufficient carbon dioxide to warrant recovery as dry ice.

Many gas streams are not always truly hydrocarbon in nature and may contain contaminants, such as carbon oxides (CO_x , where $x = 1$ and/or 2), sulfur oxides (SO_x , where $x = 2$ and/or 3), as well as ammonia (NH_3), mercaptan derivatives (RSH), carbonyl sulfide (COS), and mercaptan derivatives (RSH). The presence of these impurities may eliminate some of the sweetening processes from use since some of these processes remove considerable amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes not designed to

remove (or incapable of removing) large amounts of acid gases, whereas they are capable of removing the acid gas impurities to low levels when the acid gases are present only in low-to-medium concentration in the gas.

The sources of the various gas streams are varied but, in terms of gas cleaning (i.e., removal of the contaminants before petrochemical production), the processes are largely the same but it is a question of degree. For example, gas streams from some sources may produce gases and may contain higher amounts of carbon dioxide and/or hydrogen sulfide, and the processes will have to be selected accordingly.

In addition to its primary importance as a fuel, a gas stream – such as synthesis gas – is also a source of hydrocarbon derivatives for petrochemical feedstocks. While the major hydrocarbon constituent of a gas stream is methane, there are components such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), and mercaptan derivatives (thiols, also called mercaptans, RSH), as well as trace amounts of sundry other emissions such as carbonyl sulfide (COS). The fact that methane has a foreseen and valuable end-use makes it a desirable product, but in several other situations, it is considered a pollutant, having been identified a greenhouse gas.

In practice, heaters and scrubbers are usually installed at or near to the source. The scrubbers serve primarily to remove sand and other large-particle impurities, and the heaters ensure that the temperature of the gas does not drop too low. With gas that contains even low quantities of water, gas hydrates ($\text{C}_n\text{H}_{2n+2} \cdot x\text{H}_2\text{O}$) tend to form when temperatures drop. These hydrates are solid or semi-solid compounds, resembling ice-like crystals. If the hydrates accumulate, they can impede the passage of gas through valves and gathering systems (Zhang et al., 2007). To reduce the occurrence of hydrates, small gas-fired heating units are typically installed along the gathering pipe wherever it is likely that hydrates may form.

Gas Cleaning – Membrane Processes

Improvements in membrane technology have now made membranes competitive in other applications in the natural gas area. New membrane materials and configurations exhibit superior performance and offer improved stability against contaminants found in natural gas. The new membranes are targeted at three separations: nitrogen, carbon dioxide/hydrogen sulfide, and gas liquids. The process uses a two-step membrane system design; the methane-selective membranes do not need to be operated at low temperatures, and capital and operating costs are within economically acceptable limits.

The use of membranes has several advantages compared to the other technologies such as absorption and adsorption processes. For instance, the possibility of having a large membrane area in a small module volume due to high packing density allows lower space and weight requirements for membrane units for the same production, and consequently reduced investment. Moreover, the process is more environmentally friendly compared to the absorption process due to the non-use of chemicals. In addition to the previously mentioned advantages, membranes also have the advantage of reduced operating costs, no moving parts, and being suitable for remote locations. Its tolerance of motion makes membrane technology promising for offshore and subsea applications.

Several carbon dioxide selective membrane systems for carbon dioxide removal from natural gas have been installed onshore or topside on platforms, as listed in Table 1. For small fields with low carbon dioxide content in the gas stream, membrane systems work quite effectively, and the carbon dioxide content in the product can be quite close to the pipeline specification ($<2\%$). However, for bigger fields and high carbon dioxide content in the feed, the membrane-treated streams still have a high carbon dioxide content (e.g., $>6\%$) and need further treatment. For small fields, membrane technologies are economically competitive compared to absorption, while for large fields, absorption is still more favorable. However, due to limitations in weight and size on platforms, membrane processes can be more advantageous for offshore or subsea operations.

The membrane processes for carbon dioxide removal have been more extensively researched compared to hydrogen sulfide removal. Several commercial membrane processes for carbon dioxide removal are available. These membranes can tolerate variations in the carbon dioxide concentration in the feed stream within a large range (on the order of 3 to 90%). Also, membranes allow permeation of condensable vapors, such as C_{3+} hydrocarbon derivatives, aromatic derivatives, and water vapor, while rejecting the non-condensable gases, such as methane, ethane, nitrogen, and hydrogen. A membrane-based process for upgrading natural gas that contains C_{3+} hydrocarbon derivatives and/or acid gas is described. The conditioned natural gas can be used as fuel for gas-powered equipment, including compressors, in the gas field or the processing plant. Optionally, the process can be used to produce natural gas liquids.

Important factors for the selection of membrane material for carbon dioxide removal are high carbon dioxide permeability and carbon dioxide-methane selectivity, as well as high thermal and mechanical stability. The most commonly used commercial membranes for natural gas sweetening are cellulose acetate/triacetate and polyimide membrane. In recent years, a large number of membrane materials for carbon dioxide-methane separation have been developed and tested on a laboratory scale, including both inorganic and polymeric membrane materials.

The conventional polymeric membranes used in natural gas processing involve several challenges, typically including contamination, physical aging, and plasticization. The proper pretreatment of natural gas before membrane processes is important to avoid performance decline due to contamination; the different additives used in the oil and gas industry processing are destructive for membranes, and particles and viscous substances in the feed can block membrane pores. The main contaminants in carbon dioxide removal from natural gas are higher-molecular-weight hydrocarbon derivatives, BTEX (benzene, toluene, ethylene benzene, and xylenes), and hydrogen sulfide. The presence of higher-molecular-weight hydrocarbon derivatives in the membrane system decrease the membrane permeation ratio as the hydrocarbon derivatives slowly coat the membrane surface. The control of the humidity level of the gas is also important for some polymeric membranes, as water vapor causes swelling of the membranes and hence changes their performance.

Inorganic membranes have also been investigated for gas separation. Inorganic membranes can have higher selectivity and permeability compared to polymeric membranes. In general, inorganic membranes also have excellent resistance to harsh environments, and at high temperatures and pressures.

Gas Cleaning – Metal Oxide Processes

The use of solids for sweetening gas (typically in batch-type process) is based on adsorption of the acid gases on the surface of the solid sweetening agent, or reaction with some component on that surface. The solids processes are usually best applied to gases containing low-to-medium concentrations of hydrogen sulfide or mercaptan derivatives. The solids processes tend to be highly selective and do not normally remove significant quantities of carbon dioxide. Consequently, the regenerated hydrogen sulfide stream from the process is usually high purity and, in addition, pressure has relatively little effect on the adsorptive capacity of a sweetening agent.

See also: Iron Oxide Process, Iron Oxide Slurry Process, Iron Oxide Suspension, Iron Sponge Process.

Gas Cleaning – Methanol Based Processes

Methanol is probably one of the most versatile solvents in the natural gas processing industry. Historically, methanol was the first commercial organic physical solvent and has been used for hydrate inhibition, dehydration, gas sweetening, and liquids recovery. Most of these applications involve low temperature where methanol's physical properties are advantageous compared with other solvents that exhibit high viscosity problems or even solids formation. Operation at low temperatures tends to suppress methanol's most significant disadvantage, high solvent loss. Furthermore, methanol is relatively inexpensive and easy to produce making the solvent an attractive alternate for gas processing applications.

Methanol has favorable physical properties relative to other solvents except for vapor pressure. The benefits of the low viscosity of methanol at low temperature are manifested in the pressure drop improvement in the cold box of injection facilities and improved heat transfer. Methanol has a much lower surface tension relative to the other solvents. High surface tension tends to promote foaming problems in contactors. Methanol processes are probably not susceptible to foaming. However, the primary drawback of methanol is the high vapor pressure that is several times greater than that of the glycols or amines. To minimize methanol losses and enhance water and acid gas absorption, the absorber or separator temperatures are usually less than -20°F.

The high vapor pressure of methanol may initially appear to be a significant drawback because of high solvent losses. However, the high vapor pressure also has significant advantages. Although often not considered, lack of thorough mixing of the gas and solvent can pose significant problems. Because of the high vapor pressure, methanol is completely mixed in the gas stream before the cold box. Glycol derivatives, because they do not completely vaporize, may require special nozzles and nozzle placement in the cold box to prevent freeze-up. Solvent carry-over to other downstream processes may also represent a significant problem. Since methanol is more volatile than glycols,

amines, and other physical solvents including lean oil, methanol is usually rejected in the regeneration step of these downstream processes. The stripper concentrates the methanol in the overhead condenser where it can be removed and further purified. Unfortunately, if glycols are carried over to amine units, the glycol becomes concentrated in the solution and potentially starts to degrade and possibly dilute the amine solution.

The use of methanol has been further exploited in the development of the Rectisol process, either alone or as toluene-methanol mixtures are used to more selectively remove hydrogen sulfide and allow carbon dioxide to pass as the overhead product. Toluene has an additional advantage insofar as carbonyl sulfide (carbonyl sulfide) is more soluble in toluene than in methanol. The Rectisol process was primarily developed to remove both carbon dioxide and hydrogen sulfide (along with other sulfur-containing species) from gas streams resulting from the partial oxidation of coal, oil, and crude oil residua. The ability of methanol to absorb these unwanted components made it the natural solvent of choice. Unfortunately, at cold temperatures, methanol also has a high affinity for hydrocarbon constituents of the gas streams. For example, propane is more soluble in methanol than is carbon dioxide.

There are two versions of the Rectisol process – the two-stage and the once-through. The first step of the two-stage process is desulfurization before shift conversion; the concentrations of hydrogen sulfide and carbon dioxide are approximately 1 and 5% by volume, respectively. Regeneration of the methanol following the desulfurization of the feed gas produces high sulfur feed for sulfur recovery. The once-through process is only applicable for high pressure partial oxidation products. The once-through process is also applicable when the hydrogen sulfide to carbon dioxide content is unfavorable, in the neighborhood of 1:50.

The physical/chemical combined purification process in which the alkanolamine (mono- or di-ethanol amine) mixed with methanol are more successful than a single physical solvent used in many of the gas treatment plants. The main advantage of this solvent lies in the good physical absorption of physical solvent component in combination with the chemical reaction of the amine. The combination of a chemically active amine with a low boiling point polar physical solvent such as methanol offers major advantages in the absorption of carbon dioxide and sulfur components as: (i) low sulfur content in the product gas, (ii) low content of carbon dioxide in the purified gas, (iii) removal by absorption of trace components, such as hydrogen cyanide, carbonyl sulfide, mercaptan derivatives, and higher-molecular-weight hydrocarbon derivatives, (iv) relative low regeneration temperature since methanol has a boiling point lower than the boiling point of water, and (v) the solvent is non-corrosive so that carbon steel equipment can be used.

A process using methanol has been developed in which there is a simultaneous capability to dehydrate, to remove acid gas, and to control hydrocarbon dew point. The IFPEXOL-1 is used for water removal and hydrocarbon dew point control; the IFPEXOL-2 process is used for acid gas removal. The novel concept behind the IFPEXOL-1 process is to use a portion of the water-saturated inlet feed to recover the methanol from the aqueous portion of the low temperature separator. That approach has solved a major problem with methanol injection in large facilities, the methanol recovery via distillation. Beyond that very simple discovery, the cold section of the process is remarkably similar to a basic methanol injection process. Modifications to the process include water washing the hydrocarbon liquid from the low temperature separator to enhance the methanol recovery. The IFPEXOL-2 process for acid gas removal is very similar to an amine-type process except for the operating temperatures. The absorber operates below -20°F to minimize methanol losses, and the regenerator operates at approximately 90 psi. Cooling is required on the regenerator condenser to recover the methanol. This process usually follows the IFPEXOL-1 process, so excessive hydrocarbon absorption is not as great a problem.

See also: IFPEXOL Process, Rectisol Process.

Gas Cleaning – Molecular Sieve Processes

Molecular sieves can be used for removal of sulfur compounds from gas streams. Hydrogen sulfide can be selectively removed to meet 4 ppm v/v specification. The sieve bed can be designed to dehydrate and sweeten simultaneously. In addition, molecular sieve processes can be used for removal of carbon dioxide from gas streams.

Molecular sieves are a crystalline form of alkali metal (calcium or sodium) alumina-silicates, similar to natural clay minerals. They are highly porous, with a very narrow range of pore sizes, and high surface area. Manufactured by ion-exchange, molecular sieves are the most expensive adsorbents and possess highly localized polar charges on their surface that act as extremely effective adsorption sites for polar compounds such as water and hydrogen sulfide. Molecular sieves are alkaline and subject to attack by acids, but special acid-resistant sieves are available for very sour gases.

In a molecular sieve, the pore openings in a given structural are all the same size and are determined by the molecular structure of the crystal and the size of molecules present in the crystal. The pores are formed by driving off water of crystallization that is present during the synthesis process. Also, molecular sieves have the large surface area typical of any solid adsorbent; however, molecular sieves have highly localized polar charges. These localized charges are the reason for the strong adsorption of polar or polarizable compounds on molecular sieves. This also results in much higher adsorptive capacities for these materials by molecular sieves than by other adsorbents, particularly in the lower concentration ranges.

Since the pore size range is narrow, molecular sieves exhibit selectivity toward adsorbates on the basis of their molecular size and tend not to adsorb bigger molecules such as the higher-molecular-weight hydrocarbon derivatives. The regeneration temperature is high. They can produce a water content as low as 1 ppm. Molecular sieves offer a means of simultaneous dehydration and desulfurization and are therefore the best choice for sour gases.

Molecular sieves are highly selective for the removal of hydrogen sulfide (as well as other sulfur compounds) from gas streams and over continuously high absorption efficiency. They are also an effective means of water removal and thus offer a process for the simultaneous dehydration and desulfurization of gas. Gas that has excessively high water content may require upstream dehydration, however.

The molecular sieve process is similar to the iron oxide process. Regeneration of the bed is achieved by passing heated clean gas over the bed. As the temperature of the bed increases, it releases the adsorbed hydrogen sulfide into the regeneration gas stream. The sour effluent regeneration gas is sent to a flare stack, and up to 2% of the gas seated can be lost in the regeneration process. A portion of the natural gas may also be lost by the adsorption of hydrocarbon components by the sieve. In this process, unsaturated hydrocarbon components, such as olefins and aromatics, tend to be strongly adsorbed by the molecular sieves.

Molecular sieves are susceptible to poisoning by such chemicals as glycols and require thorough gas cleaning methods before the adsorption step. Alternatively, the sieve can be offered some degree of protection by the use of a guard bed in which a less expensive catalyst is placed in the gas stream before contact of the gas with the sieve, thereby protecting the catalyst from poisoning.

Regeneration of a molecular sieve bed concentrates the hydrogen sulfide into a small regeneration stream which must be treated or sent to disposal. During the regeneration cycle, the hydrogen sulfide will exhibit a peak concentration in the regeneration gas and the peak is approximately 30 times the concentration of the hydrogen sulfide in the inlet stream.

See also: Attrition Catalyst, Guard Bed.

Gas Cleaning – Physical Solvent Processes

Two of the currently most-widely-used physical solvent processes for gas cleaning are Selexol process and the Rectisol process. The process solvent is a mixture of dimethyl ethers of polyethylene glycol [$\text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$] where n is between 3 and 9. The solvent is chemically and thermally stable and has a low vapor pressure that limits its losses to the treated gas. The solvent has a high solubility for carbon dioxide, hydrogen sulfide, and carbonyl sulfide. It also has appreciable selectivity for hydrogen sulfide over carbon dioxide.

The principal benefits of physical solvents are: (i) high selectivity for hydrogen sulfide over carbonyl sulfide and carbon dioxide, (ii) high loadings at high acid gas partial pressures, (iii) solvent stability, and (iv) low heat requirements because most of the solvent can be regenerated by a simple pressure letdown. The performance of a physical solvent can be easily predicted. The solubility of a compound in the solvent is directly proportional to its partial pressure in the gas phase, hence, the improvement in the performance of physical solvent processes with increasing gas pressure. Physical solvent processes can be configured to take advantage of their high hydrogen sulfide/carbon dioxide selectivity together with high levels of carbon dioxide recovery.

In the Selexol process, the solvent is composed of a dimethyl ether of polyethylene glycol, which is chemically inert and not subject to degradation. The process also removes carbonyl sulfide, mercaptan derivatives, ammonia, hydrogen cyanide, and metal carbonyl derivatives. A variety of flow schemes permit process optimization and energy reduction, and the partial pressure of the acid gas is the key driving force. Typical feedstock conditions range between 300 and 2,000 psia, with acid composition (carbon dioxide plus hydrogen sulfide) from 5% v/v to more than 60% v/v by volume. The product specifications achievable depend on the application and can range from ppm up to percent levels of acid gas.

The Selexol process can be configured in various ways, depending on the requirements for the level of hydrogen sulfide/carbon dioxide selectivity, the depth of sulfur removal, the need for bulk carbon dioxide removal, and whether the gas needs to be dehydrated. The gas stream from the low-pressure flash is combined with the acid gas from the regenerator. This combined gas stream is then sent to a sulfur recovery unit. However, the hydrogen sulfide content could be too low for use in a conventional Claus process. The Selexol process can, however, be configured to give both a rich acid gas feed to the Claus unit as well as to provide for bulk carbon dioxide removal.

The Rectisol process is the most widely used physical solvent gas treating process for acid gas removal using an organic solvent at low temperatures. In general, methanol is used for removal of hydrogen sulfide, carbonyl sulfide, and carbon dioxide as well as removal of organic and inorganic impurities. It is possible to produce a clean gas with less than 0.1 ppm sulfur and a carbon dioxide content down to the ppm range. The main advantage over other processes is the use of a cheap, stable and easily available solvent, a very flexible process and low utilities.

The process is designed for the bulk removal of carbon dioxide and nearly all of the removal of hydrogen sulfide and carbonyl sulfide takes place in the bottom section of the absorber. The methanol solvent contacting the feed gas in the first stage of the absorber is stripped in two stages of flashing via pressure reduction. The regenerated solvent is virtually free of sulfur compounds but contains some carbon dioxide. The acid gas leaving the first stage solvent regenerator is suitable for a Claus plant. The second stage of absorption is designed for the removal of the remaining sulfur compounds and carbon dioxide. The solvent from the bottom of the second stage of the absorber is stripped deeply in a steam-heated regenerator and is returned to the top of the absorption column after cooling and refrigeration.

See also: Rectisol Process, Selexol Process, Sulfinol Process.

Gas Cleaning – Process Selection

Each of the gas cleaning processes has advantages relative to the others for certain applications; therefore, in selection of the appropriate process, the following facts should be considered: (i) tail gas clean-up requirements, (ii) type and concentration of impurities in the sour gas, (iii) specifications for the residue gas, (iv) specifications for the acid gas, (v) temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered, (vi) volume of gas to be processed, (vii) hydrocarbon composition of the gas, and (viii) selectivity required for acid gas removal.

Furthermore, technologies in gas processing that have evolved considerably in the last four decades and have moved toward major trends in natural gas processing in the 21st century. These technologies have arisen to allow a much more rigorous optimization of several variables such as: (i) operational flexibility, and (ii) the types of gas that are offered from processing. Also, increased attention to thermodynamic efficiency and better use of refrigeration and recompression since 1980 have led to development of enhanced recovery processes for natural gas liquids.

Thus, the selection of an optimum process will depend on conditions and composition of the inlet gas, cost of fuel and energy, product specifications, and relative product values.

Decisions in selecting a gas treating process can many times be simplified by gas composition and operating conditions. High partial pressures (50 psi) of acid gases enhance the probability of using a physical solvent. The presence of significant quantities of higher-molecular-weight hydrocarbon derivatives in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating.

In general, the batch and amine processes are used for over 90% of all onshore wellhead applications. Amine processes are preferred when the lower operating cost, the chemical cost for this process, is prohibitive, and justifies the higher equipment cost. The key is the sulfur content of the feed gas where below 20-pound sulfur per day, batch processes are more economical, and over 100-pound sulfur per day amine solutions are preferred.

One important aspect of gas processing that is not typically is the process for extraction (separation) of helium from gas stream. At present, there are a variety of techniques for separating and recovering helium from helium-bearing gas mixtures. Such techniques include (i) membrane technique, (ii) pressure swing adsorption technique, and (iii) cryogenic technique. Among these techniques, cryogenic processes are the most economical method and have been commonly used to produce helium at high recovery and/or purity from natural gas streams or other gas streams containing low purity helium. However, due to the standard boiling temperatures of methane, nitrogen, hydrogen, and helium, condensation-based distillation or an integrated process involving condensation, distillation, and cryogenics can be used to extract helium from natural gas streams. To meet the high requirements of the

product purities, the separation between methane and nitrogen by distillation process leaves the methane and other hydrocarbon derivatives the bottom product, while the overhead gas, which is the mixture of nitrogen, helium and hydrogen, can be further separated by cryogenic condensation process.

See also: Gas Cleaning – Process Types.

Gas Cleaning – Process Types

A gas stream gas can also be upgraded to pipeline-quality gas, and this upgraded gas may be used for residential heating and as vehicle fuel. When distributing the gas stream using pipelines, gas pipeline standards will, more than likely, become applicable. Removing water vapor is easier than removing carbon dioxide and hydrogen sulfide from the gas stream (Table G-2). A condensate trap at a proper location on the gas pipeline can remove water vapor as warm the gas stream cools by itself after leaving the digester or the gas-generating equipment.

Table G-2 Common methods for the removal of carbon dioxide and hydrogen sulfide from gas streams.

Carbon dioxide removal	Description
Water scrubbing	Uses principle of the higher solubility of carbon dioxide in water to separate the carbon dioxide from the gas. The process uses high pressure and removes hydrogen sulfide as well as carbon dioxide. The main disadvantage of this process is that it requires a large volume of water that must be purified and recycled.
Polyethylene glycol scrubbing	This process is more efficient than water scrubbing. It also requires the regeneration of a large volume of polyethylene glycol.
Chemical absorption	Chemical reaction between carbon dioxide and amine-based solvents (olamines).
Carbon molecular sieves	Uses differential adsorption characteristics to separate methane and carbon dioxide, which is carried out at high pressure (pressure swing adsorption). Hydrogen sulfide should be removed before the adsorption process.
Membrane separation	Selectively separates hydrogen sulfide from carbon dioxide from methane. The carbon dioxide and the hydrogen sulfide dissolve, while the methane is collected for use.
Cryogenic separation	Cooling until condensation or sublimation of the carbon dioxide.
Hydrogen sulfide removal	
Biological desulfurization	Natural bacteria can convert hydrogen sulfide into elemental sulfur in the presence of oxygen and iron. This can be done by introducing a small amount (2 to 5%) of air into the head space of the digester. As a result, deposits of elemental sulfur will be formed in the digester. This process may be optimized by a more sophisticated design where air is bubbled through the digester feed material. It is critical that the introduction of the air be carefully controlled to avoid reducing the amount of gas that is produced.
Iron/iron oxide reaction	Hydrogen sulfide reacts readily with either iron oxide or iron chloride to form insoluble iron sulfide. The reaction can be exploited by adding the iron chloride to the digester feed material or passing the gas through a bed of iron oxide-containing material. The iron oxide media needs to be replaced periodically. The regeneration process is highly exothermic and must be controlled to avoid problems.
Activated carbon	Activated carbon impregnated with potassium iodide can catalytically react with oxygen and hydrogen sulfide to form water and sulfur. The activated carbon beds need regeneration or replacement when saturated.
Scrubbing/membrane separation	The carbon dioxide and hydrogen sulfide can be removed by washing with water, glycol solutions, or separated using the membrane technique.

Gas processing involves the use of several different types of processes to remove contaminants from gas streams, but there is always overlap between the various processing concepts. In addition, the terminology used for gas processing can often be confusing and/or misleading because of the overlap. Gas processing is necessary to ensure that the gas prepared for transportation (usually by pipeline) and for sales must be as clean and pure as the specifications dictate. Thus, a gas stream, as it is used by consumers, is much different from the gas that is brought from, for example, the anaerobic digester. Moreover, although gas produced in the digester may be composed primarily of methane, it is by no means as pure.

The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems. In many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form. In addition to the corrosion of equipment by acid gases, the escape into the atmosphere of sulfur-containing gases can eventually lead to the formation of the constituents of acid rain, i.e., the oxides of sulfur (sulfur dioxide, SO_2 , and sulfur trioxide, SO_3). Similarly, the nitrogen-containing gases can also lead to nitrous and nitric acids (through the formation of the oxides NO_x , where $x = 1$ or 2) which are the other major contributors to acid rain. The release of carbon dioxide and hydrocarbon derivatives as constituents of refinery effluents can also influence the behavior and integrity of the ozone layer.

However, the precise area of application of a given process is difficult to predict and define and requires careful consideration of several process factors before process selection. These factors are: (i) the types of contaminants in the gas, (ii) the concentrations of contaminants in the gas, (iii) the degree of contaminant removal desired, (iv) the selectivity of acid gas removal required, (v) the temperature of the gas to be processed, (vi) the pressure of the gas to be processed, (vii) the volume of the gas to be processed, (viii) the composition of the gas to be processed, (ix) the ratio of carbon dioxide to hydrogen sulfide ratio in the gas feedstock, and (x) the desirability of sulfur recovery due to environmental issues or economic issues.

Finally, throughout the various cleaning processes, it is important to minimize the loss of methane in order to achieve an economical viable cleaning operation. However, it is also important to minimize the methane slip since methane is a strong greenhouse gas. Thus, the release of methane to the atmosphere should be minimized by treating the off-gas, air, or water streams leaving the plant even though the methane cannot be utilized. Methane can be present in the off-gas leaving a pressure swing adsorption-column, in air from a water scrubber with water recirculation or in water in a water scrubber without water recirculation.

Gas Cleaning – Removal of Acid Gases

In addition to water removal, one of the most important parts of gas processing involves the removal of hydrogen sulfide and carbon dioxide, which are generally referred to as contaminants. Gas streams from some sources contain significant amounts of hydrogen sulfide and carbon dioxide and, analogous to natural gas that contains these same impurities, is usually referred to as sour gas. Sour gas is undesirable because the sulfur compounds it contains can be extremely harmful, even lethal, to breathe and the gas can also be extremely corrosive. The process for removing hydrogen sulfide from sour gas is commonly referred to as *sweetening* the gas. Thus, sulfur compounds, mainly hydrogen sulfide, must be removed from the synthesis gas to the best possible extent since they can poison catalysts. The methanation catalyst is particularly prone to sulfur poisoning. Regenerative sorbents (so-called sulfur guards) can be used to reduce sulfur concentrations to the necessary limits, well below 1 ppm v/v. Washing techniques (based on physical or chemical adsorption) can also be implemented, making sulfur recovery via a Claus process possible if economically viable.

There are four general processes used for emission control (often referred to in another, more specific context as flue gas desulfurization: (i) physical adsorption in which a solid adsorbent is used, (ii) physical absorption in which a selective absorption solvent is used, (iii) chemical absorption in which a selective absorption solvent is used, (iv) and catalytic oxidation thermal oxidation.

Adsorption

Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. Activated carbon and molecular sieves are also capable of adsorbing water in addition to the acid gases.

In order to avoid any confusion, it must be emphasized here that *absorption* differs from *adsorption* in that absorption is not a physical-chemical surface phenomenon but a process in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (*chemisorption*). Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. In these processes, a solid with a high surface area is used. Molecular sieves (zeolites) are widely used and are capable of adsorbing large amounts of gas. In practice, more than one adsorption bed is used for continuous operation – one bed is in use, while the other is being regenerated.

On the other hand, adsorption is usually a gas-solid interaction in which an adsorbent such as activated carbon (the *adsorbent* or *adsorbing medium*) which can be regenerated upon *desorption*. The quantity of material adsorbed is proportional to the surface area of the solid, and, consequently, adsorbents are usually granular solids with a large surface area per unit mass. Activated carbon impregnated with potassium iodide can catalytically react with oxygen and hydrogen sulfide to form water and sulfur. The reaction is best achieved at 50 to 70°C (122 to 158°F) and 100 to 120 psi. The activated carbon adsorption beds must be regenerated or replaced before they become ineffective due to over-saturation.

Regeneration is accomplished by passing hot dry fuel gas through the bed. Molecular sieves are competitive only when the quantities of hydrogen sulfide and carbon disulfide are low. The captured (adsorbed) gas can be desorbed with hot air or steam, either for recovery or for thermal destruction. Adsorber units are widely used to increase a low gas concentration prior to incineration unless the gas concentration is high in the inlet air stream, and the process is also used to reduce problem odors (or obnoxious odors) from gases. There are several limitations to the use of adsorption systems, but it is generally the case that the major limitation is the requirement for minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency.

Absorption

Absorption is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon). In addition to economic issues or constraints, the solvents used for gas processing should have: (i) a high capacity for acid gas, (ii) a low tendency to dissolve hydrogen, (iii) a low tendency to dissolve low-molecular-weight hydrocarbon derivatives, (iv) low vapor pressure at operating temperatures to minimize solvent losses, (v) low viscosity, (vi) low thermal stability, (vii) absence of reactivity toward gas components, (viii) low tendency for fouling, (ix) a low tendency for corrosion, and (x) economically acceptable.

Noteworthy commercial processes used are the Selexol process, the Sulfinol process, and the Rectisol process. In these processes, no chemical reaction occurs between the acid gas and the solvent. The solvent, or absorbent, is a liquid that selectively absorbs the acid gases and leaves out the hydrocarbons.

The Selexol process uses a mixture of the dimethyl ether of propylene glycol as a solvent. It is nontoxic, and its boiling point is not high enough for amine formulation. The selectivity of the solvent for hydrogen sulfide (H_2S) is much higher than that for carbon dioxide (CO_2), so it can be used to selectively remove these different acid gases, minimizing carbon dioxide content in the hydrogen sulfide stream sent to the sulfur recovery unit (SRU) and enabling regeneration of solvent for carbon dioxide recovery by economical flashing. In the process, a gas stream is injected in the bottom of the absorption tower operated at 1,000 psi. The rich solvent is flashed in a flash drum (flash reactor) at 200 psi where methane is flashed and recycled back to the absorber and joins the sweet (low-sulfur or no-sulfur) gas stream. The solvent is then flashed at atmospheric pressure, and acid gases are flashed off. The solvent is then stripped by steam to completely regenerate the solvent, which is recycled back to the absorber. Any hydrocarbon derivatives are condensed, and any remaining acid gases are flashed from the condenser drum. This process is used when there is a high acid gas partial pressure and there are no high-boiling hydrocarbon derivatives. Diisopropanolamine (DIPA) can be added to this solvent to remove carbon dioxide to a level suitable for pipeline transportation.

The Sulfinol process uses a solvent that is a composite solvent, consisting of a mixture of diisopropanolamine (30 to 45% v/v) or methyl diethanolamine (MDEA), sulfolane (tetrahydrothiophene dioxide) (40 to 60% v/v), and water (5 to 15% v/v). The acid gas loading of the Sulfinol solvent is higher, and the energy required for its regeneration is lower than those of purely chemical solvents. At the same time, it has the advantage over purely physical solvents that

severe product specifications can be met more easily and co-absorption of hydrocarbon derivatives is relatively low. Aromatic compounds, higher-molecular-weight hydrocarbon derivatives, and carbon dioxide are soluble to a lesser extent. The process is typically used when the hydrogen sulfide-carbon dioxide ratio is greater than 1:1 or where carbon dioxide removal is not required to the same extent as hydrogen sulfide removal. The process uses a conventional solvent absorption and regeneration cycle in which the sour gas components are removed from the feed gas by countercurrent contact with a lean solvent stream under pressure. The absorbed impurities are then removed from the rich solvent by stripping with steam in a heated regenerator column. The hot lean solvent is then cooled for reuse in the absorber. Part of the cooling may be by heat exchange with the rich solvent for partial recovery of heat energy. The solvent reclaimer is used in a small ancillary facility for recovering solvent components from higher boiling products of alkanolamine degradation or from other high-boiling or solid impurities.

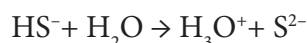
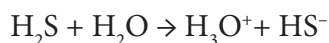
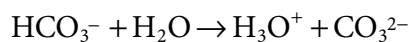
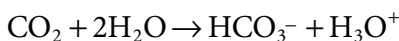
The big difference between water scrubbing and the Selexol process is that carbon dioxide and hydrogen sulfide are more soluble in Selexol which results in a lower solvent demand and reduced pumping. In addition, water and halogenated hydrocarbon derivatives (contaminants in gas streams from landfill sites) are removed when scrubbing the gas stream with Selexol in which the Selexol solvents is designed for recirculation. Due to formation of elemental sulfur stripping, the Selexol solvent with air is not recommended but with steam or inert gas (an upgraded gas stream). Removing hydrogen sulfide beforehand is an alternative.

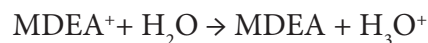
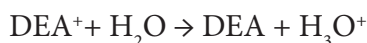
Chemisorption

Chemisorption (chemical absorption) processes are characterized by a high capability of absorbing large amounts of acid gases. They use a solution of a relatively weak base, such as monoethanolamine. The acid gas forms a weak bond with the base which can be regenerated easily. Mono- and diethanolamine derivatives are frequently used for this purpose. The amine concentration normally ranges between 15 and 30%. The gas stream is passed through the amine solution where sulfides, carbonates, and bicarbonates are formed. Diethanolamine is a favored absorbent due to its lower corrosion rate, smaller amine loss potential, fewer utility requirements, and minimal reclaiming needs. Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS), while the mono- reacts irreversibly with 95% of the carbonyl sulfide and forms a degradation product that must be disposed in an environmentally acceptable manner.

The ethanolamine process, known as the *Girbotol* process, removes acid gases (hydrogen sulfide and carbon dioxide) from gases. The Girbotol process uses an aqueous solution of ethanolamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower (the absorber) through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

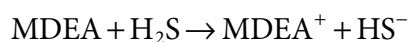
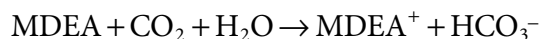
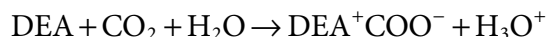
Alkanolamine scrubbers can be used to remove hydrogen sulfide or hydrogen sulfide and carbon dioxide simultaneously. For instance, monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and triethanolamine (TEA) can be used. The alkanolamine scrubbing process is also carried out in two steps: the first step involves the amine contactor, and the second step involves the regenerator. In a process with diethanolamine and methyldiethanolamine, the main reactions in equilibrium in the system are:





The pH is an important parameter because it affects the concentration of the ionic species and therefore the reactions with the amines. Moreover, the temperature and pressure also have a significant effect on the process.

The reactions that involve carbon dioxide and hydrogen sulfide with amines are as follows:



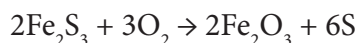
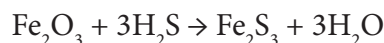
This system is complex due to the number of reactions involved, and other reactions may also occur in the system. Tertiary amines such as DMEA do not react directly with carbon dioxide, and hydrogen sulfide with amines is almost instantaneous by proton transfer. Thus, tertiary amines are used for selective hydrogen sulfide removal, and for selective hydrogen sulfide and carbon dioxide removal, a mixed amine system (tertiary and primary or secondary) is employed. Moreover, other compounds can be mixed with amine solutions.

Thus, treatment of a gas stream to remove the acid gas constituents (hydrogen sulfide and carbon dioxide) is most often accomplished by contact of the gas stream with an alkaline solution. The most commonly used treating solutions are aqueous solutions of the ethanolamine or alkali carbonates, although a considerable number of other treating agents have been developed in recent years. Most of these newer treating agents rely upon physical absorption and chemical reaction. When only carbon dioxide is to be removed in large quantities or when only partial removal is necessary, a hot carbonate solution or one of the physical solvents is the most economical selection.

The primary process for sweetening sour gas uses an amine (*olamine*) solution to remove the hydrogen sulfide (the *amine process*). The sour gas is run through a tower, which contains the olamine solution. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from the gas stream as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. The amine solution used can be regenerated for reuse and, although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponge to remove hydrogen sulfide and carbon dioxide, including bio-based iron sponge process.

Diglycolamine (DGA) is another amine solvent used in the Econamine process in which absorption of acid gases occurs in an absorber containing an aqueous solution of diglycolamine, and the heated rich solution (saturated with acid gases) is pumped to the regenerator. Diglycolamine solutions are characterized by low freezing points, which make them suitable for use in cold climates.

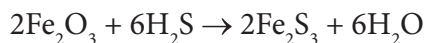
The most well-known hydrogen sulfide removal process is based on the reaction of hydrogen sulfide with iron oxide (often also called the iron sponge process or the dry box method) in which the gas is passed through a bed of wood chips impregnated with iron oxide. The iron oxide is converted to the corresponding sulfur which is reerated by oxidation:



The iron oxide process (which was implemented during the 19th century and also referred to as the iron sponge process) is the oldest and still the most widely used batch process for sweetening the gas stream. The reaction can be exploited by adding the iron chloride to the digester feed material or passing the gas stream through a bed of iron oxide-containing material. The iron oxide comes in different forms such as rusty steel wool, iron oxide pellets, or wood pellets coated with iron oxide. The iron oxide media needs to be replaced periodically. The regeneration process is highly exothermic and must be controlled to avoid problems.

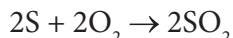
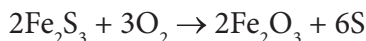
In the process, the sour gas is passed down through the bed. In the case where continuous regeneration is to be utilized, a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the on-stream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove. Ferric hydroxide $[\text{Fe}(\text{OH})_3]$ can also be used in this process.

The process is usually best applied to gases containing low-to-medium concentrations (300 ppm v/v) of hydrogen sulfide or mercaptan derivatives. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is high purity. The use of iron oxide process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:



The reaction requires the presence of slightly alkaline water and a temperature below 43°C (110°F), and bed alkalinity (pH: 8 to 10) should be checked regularly, usually on a daily basis. The pH level is maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the in-coming gas stream (i.e., the gas stream at the inlet).

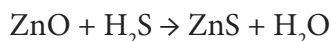
The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:



The regeneration step is exothermic, and air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly, the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles, this sulfur will form a cake over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles, the bed must be removed and a new bed introduced into the vessel.

The iron oxide process is one of several metal oxide-based processes that scavenge hydrogen sulfide and organic sulfur compounds (mercaptan derivatives) from gas streams through reactions with the solid-based chemical adsorbent. They are typically non-regenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most of the processes are governed by the reaction of a metal oxide with hydrogen sulfide to form the metal sulfide. For regeneration, the metal oxide is reacted with oxygen to produce elemental sulfur and the regenerated metal oxide. In addition, to iron oxide, the primary metal oxide used for dry sorption processes is zinc oxide.

In the zinc oxide process, the zinc oxide media particles are extruded cylinders 3-4 mm in diameter and 4 to 8 mm in length and react readily with the hydrogen sulfide:



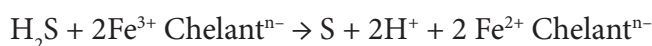
At increased temperatures (205 to 370°C, 400 to 700°F), zinc oxide has a rapid reaction rate, therefore providing a short mass transfer zone, resulting in a short length of unused bed and improved efficiency.

Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the *Ferrox* process or the Stretford process. The *Ferrox process* is based on the same chemistry as the iron oxide process except

that it is fluid and continuous. The *Stretford* process employs a solution containing vanadium salts and anthraquinone disulfonic acid.

Most hydrogen sulfide removal processes return the hydrogen sulfide unchanged, but if the quantity involved does not justify installation of a sulfur recovery plant (usually a Claus plant), it is necessary to select a process that directly produces elemental sulfur. In the Beavon-Stretford process, a hydrotreating reactor converts sulfur dioxide in the off-gas to hydrogen sulfide which is contacted with Stretford solution (a mixture of vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide) in a liquid-gas absorber. The hydrogen sulfide reacts stepwise with sodium carbonate and anthraquinone disulfonic acid to produce elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber.

Even though the removal of hydrogen sulfide can be achieved by chemical or physical absorption, chemical scrubbers are the most commonly used systems for hydrogen sulfide removal. The most important processes are iron-based chelation methods and absorption by alkanolamines. In iron-based chelation processes, there are two main reactions:



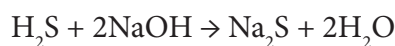
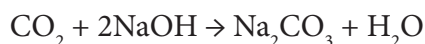
The first step involves the chemical reaction to produce elemental sulfur, and in the second step, iron(III) is regenerated. Several commercial processes are based on iron chelation, such as the Lo-cat and Sulferox processes. Ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA) are the most conventional ligands used in this process. The operating conditions are typically: 4 to 8°C (39.5 to 46.5°F), pH 4 to pH 8, iron concentration on the order of 1,000 to 10,000 ppm v/v with a chelant/iron ratio in the range 1.1 to 2.0.

The process using potassium phosphate is known as phosphate desulfurization, and it is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbon derivatives as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally. Processes using ethanolamine and potassium phosphate are now widely used.

Other Processes

There is a series of alternate processes that involve (i) the use of chemical reactions to remove contaminants from gas streams or (ii) the use of specialized equipment to physically remove contaminants from gas streams.

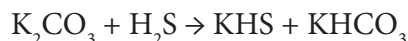
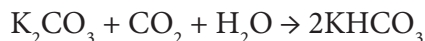
As example of the first category, i.e., the use of chemical reactions to remove contaminants from gas streams, strong basic solutions are effective solvents for acid gases. However, these solutions are not normally used for treating large volumes of a gas stream because the acid gases form stable salts, which are not easily regenerated. For example, carbon dioxide and hydrogen sulfide react with aqueous sodium hydroxide to yield sodium carbonate and sodium sulfide, respectively.



However, a strong caustic solution is used to remove mercaptans from gas and liquid streams. In the Merox Process, for example, a caustic solvent containing a catalyst such as cobalt, which is capable of converting mercaptans (RSH) to caustic insoluble disulfides (RSSR), is used for streams rich in mercaptans after removal of hydrogen sulfide. Air is used to oxidize the mercaptan derivatives to disulfide derivatives. The caustic solution is then recycled for regeneration. The Merox process is mainly used for treatment of refinery gas streams.

As one of the major contaminants in gas streams, carbon dioxide must optimally be removed as it reduces the energy content of the gas and affect the selling price of the gas. Moreover, it becomes acidic and corrosive in the presence of water that has a potential to damage the pipeline and the equipment system. Hence, the presence of carbon dioxide in gas streams remains one of the challenging gas separation problems in process engineering for carbon dioxide/methane systems. Therefore, the removal of carbon dioxide from the gas stream through the purification processes is vital for an improvement in the quality of the product.

Carbonate washing is a mild alkali process (typically, the alkali is potassium carbonate, K_2CO_3 for gas processing for the removal of acid gases (such as carbon dioxide and hydrogen sulfide) from gas streams and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature. It has been demonstrated that the process works best near the temperature of reversibility of the reactions:



The Fluor process uses propylene carbonate to remove carbon dioxide, hydrogen sulfide, carbonyl sulfide, water, and higher boiling hydrocarbon derivatives (C_2^+) from gas stream.

Water washing, in terms of the outcome, is almost analogous to (but often less effective than) washing with potassium carbonate, and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical, and there is also a relatively high absorption of hydrocarbon derivatives, which are liberated at the same time as the acid gases. The water scrubbing process uses the higher solubility of carbon dioxide in water to separate the carbon dioxide from gas stream. This process is done under high pressure and removes hydrogen sulfide as well as carbon dioxide. The main disadvantage of this process is that it requires a large volume of water that must be purified and recycled. An analogous process, polyethylene glycol scrubbing, is similar to water scrubbing, but it is more efficient. However, the process does require the regeneration of a large volume of polyethylene glycol.

In chemical conversion processes, contaminants in gas emissions are converted to compounds that are not objectionable or that can be removed from the stream with greater ease than the original constituents. For example, a number of processes have been developed that remove hydrogen sulfide and sulfur dioxide from gas streams by absorption in an alkaline solution.

Catalytic oxidation is a chemical conversion process that is used predominantly for destruction of volatile organic compounds and carbon monoxide. These systems operate in a temperature regime on the order of 205 to 595°C (400 to 1,100°F) in the presence of a catalyst – in the absence of the catalyst, the system would require a higher operating temperature. The catalysts used are typically a combination of noble metals deposited on a ceramic base in a variety of configurations (e.g., honeycomb-shaped) to enhance good surface contact. Catalytic systems are usually classified on the basis of bed types such as *fixed bed* (or *packed bed*) and *fluid bed* (*fluidized bed*). These systems generally have high destruction efficiencies for most volatile organic compounds, resulting in the formation of carbon dioxide, water, and varying amounts of hydrogen chloride (from halogenated hydrocarbon derivatives). The presence in emissions of chemicals such as heavy metals, phosphorus, sulfur, chlorine, and most halogens in the incoming air stream act as poison to the system and can foul up the catalyst. Thermal oxidation systems, without the use of catalysts, also involve chemical conversion (more correctly, chemical destruction) and operate at temperatures in excess of 815°C (1,500°F), or 220 to 610°C (395 to 1,100°F) higher than catalytic systems.

Other processes include the *Alkazid process* for removal of hydrogen sulfide and carbon dioxide using concentrated aqueous solutions of amino acids. The hot potassium carbonate process decreases the acid content of natural and refinery gas from as much as 50% to as low as 0.5% and operates in a unit similar to that used for amine treating. The *Giammarco-Vetrocoke* process is used for hydrogen sulfide and/or carbon dioxide removal. In the hydrogen sulfide removal section, the reagent consists of sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) or a mixture of the carbonates which contains a mixture of arsenite derivatives and arsenate derivatives; the carbon dioxide removal section utilizes hot aqueous alkali carbonate solution activated by arsenic trioxide (As_2O_3) or selenous acid (H_2SeO_3) or tellurous acid (H_2TeO_3). A word of caution might be added related to the last three chemicals which are toxic and can involve stringent environmental-related disposal protocols.

Molecular sieves are highly selective for the removal of hydrogen sulfide (as well as other sulfur compounds) from gas streams and offer continuously high absorption efficiency. They are also an effective means of water removal and thus offer a process for the simultaneous dehydration and desulfurization of gas. Gas that has excessively high water content may require upstream dehydration, however. The carbon molecular sieve method uses differential adsorption characteristics to separate methane and carbon dioxide.

In addition, the molecular sieve process is similar to the iron oxide process. Regeneration of the bed is achieved by passing heated clean gas over the bed. As the temperature of the bed increases, it releases the adsorbed hydrogen sulfide and the sour effluent regeneration gas is sent to a flare stack, and up to 2% v/v of the gas seated can be lost in the regeneration process. A portion of the gas stream may also be lost by the adsorption of hydrocarbon components by the sieve.

In this process, unsaturated hydrocarbon components, such as olefin derivatives and aromatic derivatives, tend to be strongly adsorbed by the molecular sieve. Molecular sieves are susceptible to poisoning by such chemicals as glycols and require thorough gas cleaning methods before the adsorption step. Alternatively, the sieve can be offered some degree of protection by the use of *guard beds* in which a less expensive catalyst is placed in the gas stream before contact of the gas with the sieve, thereby protecting the catalyst from poisoning. This concept is analogous to the use of guard beds or attrition catalysts in the crude oil industry.

Carbon molecular sieves are excellent products to separate specifically a number of different gaseous compounds in the gas stream. Thereby, the molecules are usually loosely adsorbed in the cavities of the carbon sieve but not irreversibly bound. The selectivity of adsorption is achieved by different mesh sizes and/or application of different gas pressures. When the pressure is released, the compounds extracted from the gas stream are desorbed. The process – pressure swing adsorption (PSA) technology – can be used to enrich methane from the gas stream in which the molecular sieve is applied which is produced from coke rich in pores in the micrometer range. The pores are then further reduced by cracking of the hydrocarbon derivatives.

In order to reduce the energy consumption for gas compression, a series of vessels are linked together. The gas pressure released from one vessel is subsequently used by the others. Usually four vessels in series are used filled with the molecular sieve which removes at the same time carbon dioxide and any water vapor. After removal of hydrogen sulfide, i.e., using activated carbon and water condensation in a cooler at 4°C, the gas stream flows at a pressure of 90 psi into the adsorption unit. The first column cleans the raw gas at 90 psi to an upgraded gas stream with a vapor pressure of less than 10 ppm water and a methane content of 96 % or more.

In the second column, the pressure of 90 psi is first released to approximately 45 psi by pressure communication with column 4, which was previously degassed by a slight vacuum. In a second step, the pressure is then reduced to atmospheric pressure. The released gas flows back to the digester in order to recover the methane. The third column is evacuated from 15 psi to 0.15 psi. The desorbed gas consists predominantly of carbon dioxide but also some methane and is therefore normally released to the environment. In order to reduce methane losses, the system can be designed with recirculation of the desorbed gases.

A number of other possible impurities, such as organic acids (e.g., formic and acetic acid) and unsaturated and higher boiling hydrocarbon derivatives, are normally not included in purity specifications for synthesis processes because they are already undesirable in upstream process stages of synthesis gas production (e.g., compression steps). However, organic compounds present must be below their dewpoint at pressure of the gas application to prevent condensation and fouling in the system. For organic compounds with sulfur or nitrogen heteroatoms (such as thiophene derivatives and pyridine derivatives), the additional specification applies that they need to be removed below ppm v/v level, as they are intrinsically poisonous for the catalyst.



Thiophene



Pyridine

Gas Cleaning – Removal of Alkali Metal Salts

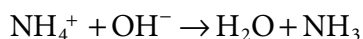
Compared with fossil fuels, biomass is rich in alkali salts that typically vaporize at high gasifier temperatures but condense downstream below 600°C (1110°F). Methods are available to strip the alkali contents since condensation of alkali salts can cause serious corrosion problems. The alkali will condense onto fine solid particles and can be subsequently captured in a cyclone, electrostatic precipitators, or filters when the gas temperature is below 600°C (1,110°F). The hot gas can also be passed through a bed of active bauxite to remove alkali when cooling of gas is not permitted.

Gas Cleaning – Removal of Ammonia

Biomass with a relatively high nitrogen content will generate a product gas that contains ammonia (NH₃) and hydrogen cyanide (HCN) (Yuan et al., 2010) which, in turn, will generate nitrogen oxides (NO_x) during combustion. In the case of the gasification of biomass (to produce a gaseous product), the concentration of ammonia in the product gas depends not only on the nature of the biomass feedstock used but also on the gasifier design parameters and operating conditions.

Ammonia can be removed by wet scrubbing technology which has been widely adopted in the existing biomass gasification processes (Dou et al., 2002; Proell et al., 2005), and the ammonia can be removed when the gas is dried. As a result, a separate cleaning step is therefore usually not necessary.

Ammonia removal (often referred to as ammonia stripping) stripping is a desorption process used to lower the ammonia content of a wastewater stream. Some wastewaters contain large amounts of ammonia and/or nitrogen-containing compounds that may readily form ammonia. It is often easier and less expensive to remove nitrogen from wastewater in the form of ammonia than to convert it to nitrate-nitrogen before removal. Ammonia (a weak base) reacts with water (a weak acid) to form ammonium hydroxide. In ammonia stripping, lime or caustic is added to the wastewater until the pH reaches 10.8 to 11.5 standard units which converts ammonium hydroxide ions to ammonia gas according to the following reaction(s):



There are two process variations for ammonia stripping: the cross-flow tower, and (ii) the countercurrent tower. In a cross-flow tower, the solvent gas (air) enters along the entire depth of fill and flows through the packing, as the alkaline wastewater flows downward. In the countercurrent tower, air is drawn through openings at the bottom, as wastewater is pumped to the top of a packed tower. Free ammonia (NH₃) is stripped from falling water droplets into the air stream, then discharged to the atmosphere.

Compared with wet scrubbing technology, hot-gas cleanup technology, preferably employing catalysts, is more advantageous with respect to energy efficiencies as it eliminates the needs of cooling the product gas and re-heating again for the synthesis gas applications. Catalytic processes effectively remove ammonia by converting it to nitrogen, hydrogen, and water. Nickel-Ni-based catalysts have higher activity, while other catalysts do not have good potentials for ammonia.

See also: Gas Cleaning.

Gas Cleaning – Removal of Condensable Hydrocarbons

Hydrocarbon derivatives that are higher molecular weight than methane that are present in the gas streams are valuable raw materials and important fuels. They can be recovered by lean oil extraction. The first step in this process is to cool the treated gas by exchange with liquid propane, after which the cooled gas is then washed with a cold hydrocarbon liquid, which dissolves most of the condensable hydrocarbon derivatives. The uncondensed gas is a dry gas stream and is composed mainly of methane. The dry gas stream may then be used either as a fuel or as a chemical

feedstock. Another way to recover any higher-molecular-weight hydrocarbon constituents from a gas stream is by using cryogenic cooling (cooling to low temperatures on the order of -100 to -115°C (-150 to -175°F), which are achieved primarily through lowering the temperatures to below the dew point.

To prevent hydrate formation, gas stream may be treated with glycols, which dissolve water efficiently. Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) are typical solvents for water removal. Triethylene glycol is preferable in vapor phase processes because of its low vapor pressure, which results in less glycol loss. The triethylene glycol absorber unit typically contains 6 to 12 bubble-cap trays to accomplish the water absorption. However, more contact stages may be required to reach dew points below -40°C (-40°F). Calculations to determine the number of trays or feet of packing, the required glycol concentration, or the glycol circulation rate require vapor-liquid equilibrium data. In addition, predicting the interaction between triethylene glycol and water vapor in the gas stream over a broad range allows the designs for ultra-low dew point applications to be made.

One alternative to using bubble-cap trays is the use of the adiabatic expansion of the inlet gas. In the process, the inlet gas is first treated to remove water and acid gases, then cooled via heat exchange and refrigeration. Further cooling of the gas is accomplished through turbo expanders, and the gas is sent to a demethanizer to separate methane from the higher-boiling hydrocarbon derivatives. Improved recovery of the higher-boiling hydrocarbon derivatives could be achieved through better control strategies and by use of on-line gas chromatographic analysis.

Membrane separation process are very versatile and are designed to process a wide range of feedstocks and offer a simple solution for removal and recovery of higher boiling hydrocarbon derivatives from gas streams. There are two membrane separation techniques: (i) high pressure gas separation and (ii) gas-liquid adsorption. The high pressure separation process selectively separates hydrogen sulfide and carbon dioxide from methane. Usually, this separation is performed in three stages and produces methane with a high degree of purity (on the order of 96% v/v methane).

The separation process is based on high-flux membranes that selectively permeates higher boiling hydrocarbon derivatives (compared to methane) and are recovered as a liquid after recompression and condensation. The residue stream from the membrane is partially depleted of higher boiling hydrocarbon derivatives, and is then sent to a sales gas stream. Gas permeation membranes are usually made with vitreous polymers that exhibit good selectivity, but, to be effective, the membrane must be very permeable with respect to the separation process.

Membrane separation is based on the selectivity properties of the membrane material. The driving force is the difference in chemical potential, which includes the effect of temperature and partial pressure regimes. Membranes can be operated at high pressure (>300 psi) or low pressure (120 to 150 psi). Several membranes can be used for gas stream upgrading, and these can be classified by the type of material: non-polymeric membranes (such as alumina, zeolites, and carbon), ceramic membranes, palladium membranes, and carbon molecular sieve membranes. Nevertheless, polymeric membranes are the most widely used because they are cheaper than inorganic membranes. Moreover, polymeric materials can be easily fabricated into flat sheets or asymmetric hollow fibers, both shapes that are usually used in industrial applications.

The material properties that define the performance are molecular structure, glass transition temperature, crystallinity, and degree of crosslinking. However, commercially available polymeric membranes are usually degraded by hydrogen sulfide, siloxanes, and/or volatile organic compounds. For instance, hydrogen sulfide can cause plasticization of glassy polymeric membranes, and this alters the polymeric structure and weakens the mechanical strength of the membrane.

In the high-pressure separation option, pressurized gas (36 bar) is first cleaned over, for example, an activated carbon bed to remove (halogenated) hydrocarbon derivatives and hydrogen sulfide from the raw gas as well as oil vapor from the compressors. The carbon bed is followed by a particle filter and a heater. The membranes made of acetate-cellulose separate small polar molecules such as carbon dioxide, moisture, and the remaining hydrogen sulfide.

The raw gas is upgraded in 3 stages to a clean gas with 96 % methane or more. The waste gas from the first two stages is recycled, and the methane can be recovered. The waste gas from stage 3 (and in part of stage 2) is flared or used in a steam boiler as it still contains 10 to 20 % v/v methane. First experiences have shown that the membranes can last up to 3 years which is comparable to the lifetime of membranes for gas purification – a primary market for membrane technology – which last typically two to five years.

The clean gas is further compressed up to 3,600 psi and stored in steel cylinders in high, medium, and low pressure banks. The membranes are specific for given molecules, i.e., hydrogen sulfide and carbon dioxide are upgraded

in different modules. The utilization of hollow-fiber membranes allows the construction of very compact modules working in cross flow.

The gas-liquid absorption membrane method is a separation technique which was developed for gas stream upgrading only recently. The essential element is a microporous hydrophobic membrane separating the gaseous from the liquid phase. The molecules from the gas stream, flowing in one direction, which are able to diffuse through the membrane will be absorbed on the other side by the liquid flowing in countercurrent.

The absorption membranes work at approx. atmospheric pressure (1 bar) which allows low-cost construction. The removal of gaseous components is very efficient. At a temperature of 25 to 35°C (77 to 95°F), the hydrogen sulfide concentration in the raw gas of 2% v/v is reduced to less than 0.025% v/v (250 ppm v/v) – the absorbent is sodium hydroxide (NaOH) or another alkaline material. Sodium hydroxide saturated with hydrogen sulfide can be used in water treatment to remove heavy metals. The concentrated hydrogen sulfide solution is fed into a Claus reaction or oxidized to elementary sulfur. The gas stream is upgraded very efficiently from 55% v/v methane (43% v/v carbon dioxide) to more than 96% methane. The amine solution is regenerated by heating, and the carbon dioxide released is pure and can be sold for industrial applications.

The main advantages of membranes are (i) safety and simplicity of operation, (ii) relative ease of maintenance and scale-up, (iii) excellent reliability, (iv) small footprint, and (v) operation without hazardous chemicals. Several operation modes can be employed – as an example, gas stream upgrading can be achieved by a two-stage cascade process with recycling and a single stage provided good flexibility for integration into upgraded gas streams.

Extraction

There are two principle techniques for removing higher-boiling hydrocarbon constituents from gas streams and are (i) the absorption method and (ii) the cryogenic expander process. In the latter process (the cryogenic expander process), a turboexpander is used to produce the necessary refrigeration and low temperatures, and high recovery of the low-boiling constituents, such as ethane and propane, can be attained. The gas stream is first dehydrated using a molecular sieve followed by cooling of the dry stream. The separated liquid containing most of the high-boiling fractions is then demethanized, and the cold gases are expanded through a turbine that produces the desired cooling for the process. The expander outlet is a two-phase stream that is fed to the top of the demethanizer column. This serves as a separator in which: (i) the liquid is used as the column reflux and the separator vapors combined with vapors stripped in the demethanizer are exchanged with the feed gas, and (ii) the heated gas, which is partially recompressed by the expander compressor, is further recompressed to the desired distribution pressure in a separate compressor.

The extraction of higher-boiling hydrocarbon constituents from the gas stream produces both a cleaner, purer gas stream, as well as the valuable hydrocarbon derivatives for use in, say, a petrochemical plant. This process allows for the recovery of approximately 90 to 95% v/v of the ethane originally in the gas stream. In addition, the expansion turbine is able to convert some of the energy released when the gas stream is expanded into recompressing the gaseous methane effluent, thus saving energy costs associated with extracting ethane.

Absorption

The absorption method of high-molecular-weight recovery of hydrocarbon derivatives is similar to using absorption for dehydration. The main difference is that, in the absorption of higher-boiling hydrocarbon constituents from the gas stream, absorbing oil is used as opposed to glycol. This absorbing oil has an affinity for the higher-boiling hydrocarbon constituents in much the same manner as glycol has an affinity for water. Before the oil has picked up any higher-boiling hydrocarbon constituents, it is termed *lean* absorption oil.

The *oil absorption process* involves the countercurrent contact of the lean (or stripped) oil with the incoming wet gas with the temperature and pressure conditions programmed to maximize the dissolution of the liquefiable components in the oil. The *rich* absorption oil (sometimes referred to as *fat* oil), containing higher-boiling hydrocarbon constituents, exits the absorption tower through the bottom. It is now a mixture of absorption oil, propane, butanes, pentanes, and other higher-boiling hydrocarbon derivatives. The rich oil is fed into lean oil stills, where the mixture is heated to a temperature above the boiling point of the higher-boiling hydrocarbon constituents but below that of the oil. This process allows for the recovery of higher-boiling constituents from the gas stream.

The basic absorption process is subject to modifications that improve process effectiveness and even to target the extraction of specific higher-boiling hydrocarbon constituents. In the refrigerated oil absorption method, where the lean oil is cooled through refrigeration, propane recovery can be on the order of 90%+ v/v and approximately 40% v/v of the ethane can be extracted from the gas stream. Extraction of the other, higher-boiling hydrocarbon constituents is typically near-quantitative using this process.

Fractionation

Fractionation processes are similar to those processes classed as *liquids removal* processes but often appear to be more specific in terms of the objectives: hence the need to place the fractionation processes into a separate category. The fractionation processes are those processes that are used (i) to remove the more significant product stream first, or (ii) to remove any unwanted low-boiling constituents from the higher-boiling liquid products.

In the general practice of gas processing, the first unit is a de-ethanizer followed by a depropanizer then by a debutanizer and, finally, a butane fractionator. Thus, each column can operate at a successively lower pressure, thereby allowing the different gas streams to flow from column to column by virtue of the pressure gradient, without necessarily the use of pumps. The purification of hydrocarbon gases by any of these processes is an important part of gas processing operations.

Thus, after any higher-boiling hydrocarbon constituents have been removed from the gas stream, they must be separated (fractionated) into the individual constituents prior to sales. The process of fractionation occurs in stages with each stage involving separation of the hydrocarbon derivatives as individual products. The process commences with the removal of the lower-boiling hydrocarbon derivatives from the feedstock. The particular fractionators are used in the following order: (i) the de-ethanizer, which is used to separate the ethane from the stream from the gas stream, (ii) the depropanizer, which is used to separate the propane from the de-ethanized gas stream, (iii) the debutanizer, which is used to separate the butane isomers, leaving the pentane isomers and higher-boiling hydrocarbon derivatives in the gas stream, and (iv) the butane splitter or de-isobutanizer, which is used to separate n-butane and iso-butane.

After the recovery of the higher-boiling hydrocarbon constituents, sulfur-free dry gas (methane) may be liquefied for transportation through cryogenic tankers. Further treatment may be required to reduce the water vapor below 10 ppm and carbon dioxide and hydrogen sulfide to less than 100 and 50 ppm v/v, respectively. Two methods are generally used to liquefy the gas: (i) the expander cycle and (ii) mechanical refrigeration. In the expander cycle, part of the gas is expanded from a high transmission pressure to a lower pressure. This lowers the temperature of the gas. Through heat exchange, the cold gas cools the incoming gas, which in a similar way cools more incoming gas until the liquefaction temperature of methane is reached.

In mechanical refrigeration, a multicomponent refrigerant consisting of nitrogen, methane, ethane, and propane is used through a cascade cycle. When these liquids evaporate, the heat required is obtained from the gas, which loses energy/temperature till it is liquefied. The refrigerant gases are recompressed and recycled.

Enrichment

The gas product must meet specific quality measures in order for the pipeline grid to operate properly. Consequently, gas stream which, in most cases contains contaminants, must be processed, i.e., cleaned, before it can be safely delivered to the high-pressure, long-distance pipelines that transport the product to the consuming public. A gas stream that is not within certain specific gravities, pressures, Btu content range, or water content levels will cause operational problems, pipeline deterioration, or can even cause pipeline rupture. Thus, the purpose of *enrichment* is to produce a gas stream for sale. Therefore, the process concept is essentially the separation of higher-boiling hydrocarbon constituents from the methane to produce a lean, dry gas.

As an example, carbon dioxide is to some extent soluble in water, and therefore, some carbon dioxide will be dissolved in the liquid phase of the digester tank. In upgrading with the in situ methane enrichment process, sludge from the digester is circulated to a desorption column and then back to the digester. In the desorption column, carbon dioxide is desorbed by pumping air through the sludge. The constant removal of carbon dioxide from the sludge leads to an increased concentration of methane in the gas stream phase leaving the digester.

The gas stream received and transported must (especially in the United States and many other countries) meet the quality standards specified by pipeline. These quality standards vary from pipeline to pipeline and are usually a

function of (i) the design of the pipeline system, (ii) the design of any downstream interconnecting pipelines, and (iii) the requirements of the customer. In general, these standards specify that the gas stream should (i) be within a specific Btu content range, typically $1,035 \text{ Btu ft}^3 \pm 50 \text{ Btu ft}^3$, (ii) be delivered at a specified hydrocarbon dew point temperature level to prevent any vaporized gas liquid in the mix from condensing at pipeline pressure, (iii) contain no more than trace amounts of elements such as hydrogen sulfide, carbon dioxide, nitrogen, water vapor, and oxygen, and (iv) be free of particulate solids and liquid water that could be detrimental to the pipeline or its ancillary operating equipment. Gas processing equipment, whether in the field or at processing/treatment plants, assures that these specifications can be met.

In most cases, processing facilities extract contaminants and higher-boiling hydrocarbon derivatives from the gas stream but, in some cases, the gas processors blend some higher-boiling hydrocarbon derivatives into the gas stream in order to bring it within acceptable Btu levels. For instance, in some areas, if the produced gas (including coalbed methane) does not meet (or is below) the Btu requirements of the pipeline operator, in which case a blend of higher Btu-content gas stream or a propane-air mixture is injected to enrich the heat content (Btu value) prior for delivery to the pipeline.

The number of steps and the type of techniques used in the process of creating a pipeline-quality gas stream most often depends upon the source and makeup of the wellhead production stream. Among the several stages of gas processing are: (i) gas-oil separation, (ii) water removal, (iii) liquids removal, (iv) nitrogen removal, (v) acid gas removal, and (vi) fractionation.

In many instances, pressure relief at the wellhead will cause a natural separation of gas from oil (using a conventional closed tank, where gravity separates the gas hydrocarbon derivatives from the heavier oil). In some cases, however, a multi-stage gas-oil separation process is needed to separate the gas stream from the crude oil. These gas-oil separators are commonly closed cylindrical shells, horizontally mounted with inlets at one end, an outlet at the top for removal of gas, and an outlet at the bottom for removal of oil. Separation is accomplished by alternately heating and cooling (by compression) the flow stream through multiple steps. However, the number of steps and the type of techniques used in the process of creating a pipeline-quality gas stream most often depends upon the source and makeup of the gas stream. In some cases, several of the steps may be integrated into one unit or operation, performed in a different order or at alternative locations (lease/plant), or not required at all.

Gas Cleaning – Removal of Nitrogen

Nitrogen may often occur in sufficient quantities in gas streams and, consequently, lowers the heating value of the gas, and the nitrogen must be removed. However, it must be recognized that nitrogen removal requires liquefaction and fractionation of the entire gas stream, which may affect process economics. In some cases, the nitrogen-containing gas stream is blended with a gas having a higher heating value and sold at a reduced price depending upon the thermal value (Btu/ft^3).

For high flow-rate gas streams, a cryogenic process is typical and involves the use of the different volatility of methane (b.p. $-161.6^\circ\text{C}/-258.9^\circ\text{F}$) and nitrogen (b.p. $-195.7^\circ\text{C}/-320.3^\circ\text{F}$) to achieve separation. In the process, a system of compression and distillation columns drastically reduces the temperature of the gas mixture to a point where methane is liquefied and the nitrogen is not. On the other hand, for smaller volumes of gas, a system utilizing pressure swing adsorption is a more typical method of separation.

The pressure swing adsorption process is a fixed-bed adsorption process that is carried out at constant temperature and variable pressure. In the process, carbon dioxide is separated from the gas stream by adsorption on a surface under elevated pressure. The adsorbing material, usually activated carbon or zeolites, is regenerated by a sequential decrease in pressure before the column is reloaded again. An upgrading plant, using this technique, typically has four, six, or nine vessels working in parallel. When the adsorbing material in one vessel becomes saturated, the raw gas flow is switched to another vessel in which the adsorbing material has been regenerated. During regeneration, the pressure is decreased in several steps. The gas that is desorbed during the first and eventually the second pressure drop may be returned to the inlet of the raw gas, since it will contain some methane that was adsorbed together with carbon dioxide. The gas desorbed in the following pressure reduction step is either led to the next column, or if it is almost entirely methane-free, it is released to the atmosphere. If hydrogen sulfide is present in the raw gas, it will be

irreversibly adsorbed on the adsorbing material. In addition, water present in the raw gas can destroy the structure of the material. Therefore, hydrogen sulfide and water need to be removed before the pressure swing adsorption column.

Thus, the pressure swing adsorption process enables the separation of carbon dioxide from a gas stream. Nevertheless, pressure swing adsorption can be used for the separation of other compounds such as nitrogen, oxygen, and carbon monoxide. Several packing materials can be used for the removal of carbon dioxide, and these include zeolite, silica gel, and activate carbon. In order to be effective continuously, the pressure swing adsorption process is composed of various fixed-bed columns running in alternative cycles of adsorption, regeneration, and pressure build-up. In some cases, the regeneration step is carried out under vacuum, and this technology is known as vacuum swing adsorption (VSA), which requires a vacuum pump at the outlet.

Moreover, the regeneration step can be carried out by increasing the temperature to enhance the desorption of compounds such as hydrogen sulfide (which is strongly adsorbed on the packing material). On increasing the temperature at constant pressure, the process is also known as temperature swing adsorption (TSA). The temperature swing adsorption process is used for gas sweetening. The gas stream must be fed dry into pressure swing adsorption, vacuum swing adsorption, and temperature swing adsorption processes, and the water content must therefore be reduced prior to these treatments.

The pressure swing adsorption operation can be based on equilibrium or kinetic separation. The more strongly adsorbed and faster diffusing compounds are retained on the packing material in equilibrium and kinetic separation, respectively. Natural zeolites have been used for hydrogen sulfide and carbon dioxide removal by pressure swing adsorption with thermal desorption working at 25°C (77°F) in the pressure range 45 to 100 psi. However, variations in the concentration of carbon dioxide can affect the performance of the pressure swing adsorption process. For example, an increase of 5% in the flow rate of the carbon dioxide can lead to an increase in the temperature at the top of the packed bed – thus, the use of a thermocouple could enhance the control strategy.

Also, in pressure swing adsorption method, methane and nitrogen can be separated by using an adsorbent with an aperture size close to the molecular diameter of the larger species (the methane) which allows nitrogen to diffuse through the adsorbent. This results in a purified gas stream that is suitable for pipeline specifications. The adsorbent can then be regenerated, leaving a highly pure nitrogen stream. The pressure swing adsorption method is a flexible method for nitrogen rejection, being applied to both small and large flow rates.

Gas Cleaning – Removal of Particulate Matter

Particulate matter that is present in the product gas can also be a serious problem for some end-users, and catalysts used for cleaning product gases have been demonstrated to be negatively affected by particulate matter.

Particulate matter can be removed using standard technologies such as cyclones, filters, and separators, which also reduce the tar content of the gas stream, the extent of tar removal depending on the particle separation technology used. The presence of alkali is of particular importance because alkali can form silicates with low melting temperatures that may negatively affect the filter operation.

See also: Advanced Cycloning, Cyclone Separation.

Gas Cleaning – Removal of Siloxane Derivatives

Siloxane compounds are a subgroup of silicone derivatives containing silicon-oxygen (Si-O) bonds with organic radicals which are widely used for a variety of industrial processes. Siloxanes are used in products such as deodorants and shampoos, and can therefore be found in gas streams from sewage sludge treatment plants and in landfill gas. When siloxanes are burned, silicon oxide, a white powder, is formed which can create a problem in gas engines. Although most siloxanes disperse into the atmosphere where they are decomposed, some end up in wastewater, but more generally, siloxane derivatives generally end up as a significant component in the sludge.

As sludge undergoes anaerobic digestion, it may be subjected to temperatures up to 60°C (140°F). At this point, the siloxanes contained in the sludge will volatilize and become an unwanted constituent of the resulting gas stream.

This problem can be exacerbated by the fact that silicone-based anti-foaming agents are frequently added to the anaerobic digesters and these silicones sometimes biodegrade into siloxanes. Unfortunately, when siloxanes gasses are burned, they are usually converted into silicon dioxide particles, which are chemically and physically similar to sand.

Currently, there are six primary technologies for removing siloxanes from gas streams and include the following process options: (i) activated carbon is widely used to remove organic substances from gases and liquids due to its superior adsorbent properties, (ii) activated alumina (Al_2O_3) absorbs siloxanes from the gas stream; when the alumina becomes saturated, the absorption capability can be recovered by passing a regeneration gas through it, (iii) refrigeration with condensation in combination can be used to selectively remove specific compounds by lowering the temperature or pressure of the gas, and then allowing the compound to precipitate out to a liquid, and then settle out, (iv) synthetic resins remove volatile materials through adsorption. They can be specially formulated to remove specific classes of compounds, (v) liquid absorbents are used by a small number of landfill operators to treat the gas stream prior to use in combustion devices such as gas turbines, and (vi) membrane technology is a relatively recent development for siloxane removal; however, membranes are subject to acid deterioration from the acidic content usually found in raw gas stream. Of these technologies, activated carbon appears to be among the most dominant in the industry.

Gas Cleaning – Removal of Tar

Tar is a highly viscous liquid product (typically produced in thermal processes) that condenses in the low temperature zones of the equipment (the pyrolyzer or the gasifier), thereby interfering with the gas flow and leading to system disruption. It is, perhaps, the most undesirable product of the process and high residual tar concentrations in the can gas prevent utilization (Devi et al., 2003; Torres et al., 2007; Anis and Zainal, 2011; Huang et al., 2011). Methods for reduction or elimination of tar can be divided into two broad groups: (i) in situ tar reduction, also called primary tar reduction, which focuses on reducing or avoiding tar formation in the reactor, and (ii) post gasification tar reduction, also called or secondary tar reduction, which strips the tar from the product gas. A combination of in situ and post-gasification tar reductions can prove to be more effective than either of the single stages alone. The two basic post-gasification methods are physical removal and cracking (catalytic or thermal).

Physical Methods

In a process for the physical removal of tar, the tar is treated tar as dust particles or mist and the tar is condensed before separation. Physical tar removal can be accomplished by cyclones, barrier filters, wet electrostatic precipitators (ESPs), or wet scrubbers. The selection of the equipment application depends on the load concentrations of particulate matter (PM) and tar, particle size distribution, and particulate tolerance of downstream users.

Cyclone collectors are the most common of the inertial collector class and are effective in removing coarser fractions of particulate matter and operate by contacting the particles in the gas stream with a liquid. In principle the particles are incorporated in a liquid bath or in liquid particles which are much larger and therefore more easily collected. In the process, the particle-laden gas stream enters an upper cylindrical section tangentially and proceeds downward through a conical section. Particles migrate by centrifugal force generated by providing a path for the carrier gas to be subjected to a vortex-like spin. The particles are forced to the wall and are removed through a seal at the apex of the inverted cone. A reverse-direction vortex moves upward through the cyclone and discharges through a top center opening. Cyclones are often used as primary collectors because of their relatively low efficiency (50 to 90% is usual).

Cyclones may not be efficient when removing small tar droplets, and barrier filters are porous material which can capture a certain amount of tar when the product gas passes through the filters. As an aid, catalyst grains can be integrated as a fixed bed inside the filter to promote the simultaneous removal of particulate matter and tar.

Fabric filters are typically designed with non-disposable filter bags. As the gaseous (dust-containing) emissions flow through the filter media (typically cotton, polypropylene, fiberglass, or Teflon), particulate matter is collected on the bag surface as a dust cake. Fabric filters operate with collection efficiencies up to 99.9%, although other advantages are evident, but there are several issues that arise during use of such equipment.

Wet scrubbers are devices in which a countercurrent spray liquid is used to remove particles from an air stream. Device configurations include plate scrubbers, packed bed scrubbers, orifice scrubbers, venturi scrubbers, and spray towers, individually or in various combinations. Wet scrubbers can achieve high collection efficiencies at the expense of prohibitive pressure drops. The *foam scrubber* is a modification of a wet scrubber in which the particle-laden gas is passed through a foam generator, where the gas and particles are enclosed by small bubbles of foam.

Other methods include use of high-energy input venturi scrubbers or electrostatic scrubbers where particles or water droplets are charged, and flux force/condensation scrubbers where a hot humid gas is contacted with cooled liquid or where steam is injected into saturated gas. In the latter scrubber, the movement of water vapor toward the cold water surface carries the particles with it (diffusiophoresis), while the condensation of water vapor on the particles causes the particle size to increase, thus facilitating collection of fine particles.

Electrostatic precipitators operate on the principle of imparting an electric charge to particles in the incoming air stream, which are then collected on an oppositely charged plate across a high-voltage field. Particles of high resistivity create the most difficulty in collection. Conditioning agents such as sulfur trioxide (SO_3) have been used to lower resistivity. Important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include the use of high-voltage pulse energy to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations.

Wet electrostatic precipitator units have a high collection efficiency (on the order of 90%) over the entire range of particle size down to 0.5 μm with a very low-pressure drop. Wet scrubbers can achieve a high collection efficiency (also on the order of 90%) as well.

Thermal Methods

Cracking methods are more advantageous in terms of recovering the energy content in the tar by converting the high-molecular-weight constituents of the tar into lower-molecular-weight (gaseous) products such as hydrocarbon derivatives and hydrogen at high temperature (up to 1,200°C, 2,190°F) or catalytic reactions (up to 800°C, 1,470°F). Catalytic cracking is commercially used in many refinery plants and has been demonstrated to be one of the most effective processes for the conversion of high-molecular-weight products (such as crude oil residua, heavy crude oil, extra heavy oil, and tar sand bitumen) into gases and lower-molecular-weight distillable and liquids.

Non-metallic catalysts such as dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), calcite (CaCO_3), and zeolite and metallic catalysts such as nickel-based catalysts, nickel/molybdenum-based catalysts, nickel/cobalt-based catalysts, molybdenum-based catalysts, platinum-based catalysts, and ruthenium-based catalysts Mo, NiO, Pt and Ru have been applied to various tar conversion processes.

Tar removal can also be achieved by catalytic reforming which has the advantage of keeping the carbon contained in the tars available for further conversion to fuel. Another option to reduce the tar content of the synthesis gas is the use of catalytic bed material in the gasification reactor. Olivine sand has been shown to effectively reduce the tar content in a gas stream from steam gasification.

See also: Advanced Cycloning, Cyclone Separation.

Gas Cleaning – Sulfur Recovery Processes

Sulfur is present in many gas streams principally as hydrogen sulfide as well as sulfur-containing compounds which are converted to hydrogen sulfide during processing. The hydrogen sulfide, together with some or all of any carbon dioxide present, is removed from the natural gas or refinery gas by means of one gas treating process.

The side stream from acid gas treating units consists mainly of hydrogen sulfide or carbon dioxide. Carbon dioxide is usually vented to the atmosphere but sometimes is recovered for carbon dioxide floods. Hydrogen sulfide could be routed to an incinerator or flare, which would convert the hydrogen sulfide to sulfur dioxide. The release of hydrogen sulfide to the atmosphere may be limited by environmental regulations. There are many specific restrictions on these limits, and the allowable limits are revised periodically. In any case, environmental regulations severely restrict the amount of hydrogen sulfide that can be vented or flared in the regeneration cycle.

Most sulfur recovery processes use chemical reactions to oxidize hydrogen sulfide and produce elemental sulfur. These processes are generally based either on the reaction of hydrogen sulfide and oxygen or hydrogen sulfide and sulfur dioxide. Both reactions yield water and elemental sulfur. These processes are licensed and involve specialized catalysts and/or solvents. These processes can be used directly on the produced gas stream. Where large flow rates are encountered, it is more common to contact the produced gas stream with a chemical or physical solvent and use a direct conversion process on the acid gas liberated in the regeneration step.

See also: Claus Process, SCOT Process, Selectox Process.

Gas Cleaning – Water Removal

The relative humidity of the gas stream inside the digester is 100%, so the gas is saturated with water vapors. To protect the energy conversion equipment from wear and from eventual damage, water must be removed from the produced gas stream. The quantity of water contained by the gas stream depends on temperature. A part of the water vapor can be condensed by cooling of the gas. This is frequently done in the gas pipelines transporting the gas stream from digester to a unit in which the water condensates on the walls of the sloping pipes and can be collected in a condensation separator, at the lowest point of the pipeline.

Water in the liquid phase causes corrosion or erosion problems in pipelines and equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas. The simplest method of water removal (refrigeration or cryogenic separation) is to cool the gas to a temperature at least equal to or (preferentially) below the dew point.

In addition to separating any condensate from the wet gas stream, it is necessary to remove most of the associated water. Most of the liquid, free water associated with the extracted gas stream, is removed by simple separation methods; however, the removal of the water vapor that exists in solution in a gas stream requires a more complex treatment. This treatment consists of dehydrating the gas stream, which usually involves one of two processes: either absorption or adsorption.

Moisture may be removed from hydrocarbon gases at the same time as hydrogen sulfide is removed. Moisture removal is necessary to prevent harm to anhydrous catalysts and to prevent the formation of hydrocarbon hydrates (e.g., $C_3H_8 \cdot 18H_2O$) at low temperatures. A widely used dehydration and desulfurization process is the glycolamine process, in which the treatment solution is a mixture of ethanolamine and a large amount of glycol. The mixture is circulated through an absorber and a reactivator in the same way as ethanolamine is circulated in the Girbotol process. The glycol absorbs moisture from the hydrocarbon gas passing up the absorber; the ethanolamine absorbs hydrogen sulfide and carbon dioxide. The treated gas leaves the top of the absorber; the spent ethanolamine-glycol mixture enters the reactivator tower, where heat drives off the absorbed acid gases and water.

Absorption occurs when the water vapor is taken out by a dehydrating agent. Adsorption occurs when the water vapor is condensed and collected on the surface. In a majority of cases, cooling alone is insufficient and, for the most part, impractical for use in field operations. Other more convenient water removal options use (i) *hygroscopic* liquids (e.g., diethylene glycol or triethylene glycol) and (ii) solid adsorbents or desiccants (e.g., alumina, silica gel, and molecular sieves). Ethylene glycol can be directly injected into the gas stream in refrigeration plants.

Absorption

An example of absorption dehydration is known as *glycol dehydration* – the principal agent in this process is diethylene glycol which has a chemical affinity for water. Glycol dehydration involves using a solution of a glycol such as diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in a *contactor*. In practice, absorption systems recover 90 to 99% by volume of methane that would otherwise be flared into the atmosphere.

In the process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. The glycol solution absorbs water from the wet gas, and once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The dry gas stream is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the gas stream, is recycled through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100°C, 212°F) and glycol (204°C, 400°F) makes it relatively easy to remove water from the glycol solution.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In order to decrease the amount of methane and other compounds that would otherwise be lost, flash tank separator-condensers are employed to remove these compounds before the glycol solution reaches the boiler. The flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbon derivatives to vaporize (*flash*). The glycol solution then travels to the boiler, which may also be fitted with air- or water-cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or even before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas (such as high-boiling hydrocarbon vapors, the *Drizo process*) or vacuum distillation are recommended.

Another absorption process, the Rectisol process, is a physical acid gas removal process using an organic solvent (typically methanol) at subzero temperatures, and characteristic of physical acid gas removal processes, it can purify a gas stream down to 0.1 ppm v/v total sulfur, including hydrogen sulfide (H_2S) and carbonyl sulfide (COS), and carbon dioxide (CO_2) in the ppm v/v range. The process uses methanol as a wash solvent, and the wash unit operates under favorable at temperatures below 0°C (32°F). To lower the temperature of the feed gas temperatures, it is cooled against the cold-product streams, before entering the absorber tower. At the absorber tower, carbon dioxide and hydrogen sulfide (with carbonyl sulfide) are removed. By use of an intermediate flash, co-absorbed products such as hydrogen and carbon monoxide are recovered, thus increasing the product recovery rate. To reduce the required energy demand for the carbon dioxide compressor, the carbon dioxide product is recovered in two different pressure steps (medium pressure and lower pressure). The carbon dioxide product is essentially sulfur-free (hydrogen sulfide-free, carbonyl sulfide-free) and water free. The carbon dioxide products can be used for enhanced oil recovery (EOR) and/or sequestration or as pure carbon dioxide for other processes.

Adsorption

Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. It must be emphasized that *adsorption* differs from *absorption* in that absorption is not a physical-chemical surface phenomenon but a process in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). Dehydration using a solid adsorbent or solid-desiccant is the primary form of dehydrating the gas stream using adsorption, and usually consists of two or more adsorption towers, which are filled with a solid desiccant. Typical desiccants include activated alumina or a granular silica gel material. A wet gas stream is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower. There are several solid desiccants which possess the physical characteristic to adsorb water from the gas stream. These desiccants are generally used in dehydration systems consisting of two or more towers and associated regeneration equipment.

Molecular sieves – a class of aluminosilicates which produce the lowest water dew points and which can be used to simultaneously sweeten, dry gases and liquids – are commonly used in dehydrators ahead of plants designed to recover ethane and other higher-boiling hydrocarbon derivatives. These plants operate at very cold temperatures and require very dry feed gas to prevent formation of hydrates. Dehydration to -100°C (-148°F) dew point is possible with molecular sieves. Water dew points less than -100°C (-148°F) can be accomplished with special design and definitive operating parameters.

Molecular sieves are commonly used to selectively adsorb water and sulfur compounds from low-boiling hydrocarbon streams such as liquefied petroleum gas, propane, butane, pentane, low-boiling olefin derivatives, and alkylation feed. Sulfur compounds that can be removed are hydrogen sulfide, mercaptan derivatives, sulfide derivatives, and disulfide derivatives. In the process, the sulfur-containing feedstock is passed through a bed of sieves at ambient temperature. The operating pressure must be high enough to keep the feed in the liquid phase. The operation is cyclic in that the adsorption step is stopped at a predetermined time before sulfur breakthrough occurs. Sulfur and water are removed from the sieves by purging with fuel gas at 205 to 315°C (400 to 600°F).

Solid-adsorbent dehydrators are typically more effective than liquid absorption dehydrators (e.g., glycol dehydrators) and are usually installed as a type of straddle system along gas pipelines. These types of dehydration systems are best suited for large volumes of gas under high pressure, and are thus usually located on a pipeline

downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To regenerate and recycle the desiccant, a high-temperature heater is used to heat gas to a high temperature and passage of the heated gas stream through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further dehydration of the gas stream.

Although two-bed adsorbent treaters have become more common (while one bed is removing water from the gas, the other undergoes alternate heating and cooling), on occasion, a three-bed system is used: one bed adsorbs, one is being heated, and one is being cooled. An additional advantage of the three-bed system is the facile conversion of a two-bed system so that the third bed can be maintained or replaced, thereby ensuring continuity of the operations and reducing the risk of a costly plant shutdown.

Silica gel (SiO_2) and alumina (Al_2O_3) have good capacities for water adsorption (up to 8% by weight). Bauxite (crude alumina, Al_2O_3) adsorbs up to 6% by weight water, and molecular sieves adsorb up to 15% by weight water. Silica is usually selected for dehydration of sour gas because of its high tolerance to hydrogen sulfide and to protect molecular sieve beds from plugging by sulfur. Alumina *guard beds* serve as protectors by the act of attrition and may be referred to as an *attrition reactor* containing an *attrition catalyst* may be placed ahead of the molecular sieves to remove the sulfur compounds. Downflow reactors are commonly used for adsorption processes, with an upward flow regeneration of the adsorbent and cooling using gas flow in the same direction as adsorption flow.

Solid desiccant units generally cost more to buy and operate than glycol units. Therefore, their use is typically limited to applications such as gases having a high hydrogen sulfide content, low dew point requirements, simultaneous control of water, and hydrocarbon dew points. In processes where cryogenic temperatures are encountered, solid desiccant dehydration is usually preferred over conventional methanol injection to prevent hydrate and ice formation.

Cryogenics

Another possibility for drying a gas stream is by cooling the gas in electrically powered gas coolers, at temperatures below 10°C (50°F), which allows a lot of humidity to be removed. In order to minimize the relative humidity, but not the absolute humidity, the gas can be warmed up again after cooling, in order to prevent condensation along the gas pipelines.

Thus, cryogenic upgrading makes use of the distinct boiling/sublimation points of the different gases, particularly for the separation of carbon dioxide and methane. In the process, the raw (untreated) gas stream is cooled down to the temperatures where the carbon dioxide in the gas condenses or sublimates and can be separated as a liquid or a solid fraction, while methane accumulates in the gas phase. Water and siloxane derivatives are also removed during cooling of the gas. However, the content of methane in the gas stream affects the characteristics of the gas, i.e., higher pressures and/or lower temperatures are needed to condense or sublime carbon dioxide when it is in a mixture with methane. Cooling usually takes place in several steps in order to remove the different gases in the gas stream individually and to optimize the energy recovery.

As an example, a hot gas stream containing water and carbon dioxide can be upgraded; by cooling the gas to 40°C (104°F), most of the water is condensed. The remaining water is removed in the carbon dioxide removal step – the carbon dioxide to be removed from the gas stream to meet the specifications. The final concentration of carbon dioxide in the gas stream is determined by the specification of the Wobbe index. For carbon dioxide removal, considering the high partial pressure of carbon dioxide, both membranes and physical solvents can be chosen, where membranes are at their maximum scale and physical solvents are at their minimum scale. The main advantage of the cryogenic process is that it is possible to obtain a gas stream with high methane content of up to 99% v/v. The main disadvantage is that the upgrading process is necessary to use many of technological equipment, especially compressors, turbines, and heat exchangers. This significant demand for additional equipment can make the cryogenic separation process extremely expensive.

Methanol-Based Processes

Methanol is probably one of the most versatile solvents in the gas processing industry. Historically, methanol was the first commercial organic physical solvent and has been used for dehydration, hydrate inhibition, gas sweetening,

and liquids recovery. Most of these applications involve low temperature where the physical properties of methanol are advantageous compared with other solvents that exhibit high viscosity problems or even solids formation. Operation at low temperatures tends to suppress the most significant disadvantage of methanol – i.e., high solvent loss. Furthermore, methanol is relatively inexpensive and easy to produce, making the solvent an attractive alternate for gas processing applications.

The use of methanol has been further exploited in the development of the Rectisol process, either alone or as toluene-methanol mixtures are used to remove hydrogen sulfide more selectively and direct the carbon dioxide to the overhead product. Toluene has an additional advantage insofar as carbonyl sulfide (carbonyl sulfide) is more soluble in toluene than in methanol. The Rectisol process was primarily developed to remove both carbon dioxide and hydrogen sulfide (along with other sulfur-containing species) from gas streams resulting from the partial oxidation of coal, oil, and crude oil residues. The ability of methanol to absorb these unwanted components made it the natural solvent of choice. Unfortunately, at cold temperatures, methanol also has a high affinity for hydrocarbon constituents of the gas streams. For example, propane is more soluble in methanol than is carbon dioxide. There are two versions of the Rectisol process – the two-stage and the once-through. The first step of the two-stage process is desulfurization before shift conversion; the concentrations of hydrogen sulfide and carbon dioxide are approximately 1 and 5% v/v, respectively. Regeneration of the methanol following the desulfurization of the feed gas produces high sulfur feed for sulfur recovery. The once-through process is only applicable for high pressure partial oxidation products. The once-through process is also applicable when the hydrogen sulfide to carbon dioxide content is unfavorable, in the neighborhood of 1:50.

Recently, a process using methanol has been developed in which it has the simultaneous capability to dehydrate, to remove acid gas, and to control hydrocarbon dew point. The IFPEXOL-1 is used for water removal and hydrocarbon dew point control; the IFPEXOL-2 process is used for acid gas removal. The novel concept behind the IFPEXOL-1 process is to use a portion of the water-saturated inlet feed to recover the methanol from the aqueous portion of the low temperature separator. That approach has solved a major problem with methanol injection in large facilities, the methanol recovery via distillation. Beyond that discovery, the cold section of the process is remarkably similar to a basic methanol injection process. Modifications to the process include water washing the hydrocarbon liquid from the low temperature separator to enhance the methanol recovery. The IFPEXOL-2 process for acid gas removal is similar to an amine-type process except for the operating temperatures. The absorber operates below -20°F to minimize methanol losses, and the regenerator operates at approximately 90 psi. Cooling is required on the regenerator condenser to recover the methanol. This process usually follows the IFPEXOL-1 process, so excessive hydrocarbon absorption is not as great a problem.

See also: Absorption, Adsorption.

Gas Compression

Compression is used in all aspects of the gas industry, and the benefits of operating at higher pressures include the ability to transmit larger volumes of gas through a given size of pipeline, lower transmission losses due to friction, and the capability to transmit gas over long distances without additional boosting stations. In gas transmission, two basic types of compressors are used: reciprocating and centrifugal compressors. Reciprocating compressors are usually driven by either electric motors or gas engines, whereas centrifugal compressors use gas turbines or electric motors as drivers.

The key variables for equipment selections are life cycle cost, capital cost, maintenance costs, including overhaul and spare parts, fuel, or energy costs. The units' level of utilization, as well as demand fluctuations, plays an important role. While both gas engines and gas turbines can use pipeline gas as a fuel, an electric motor has to rely on the availability of electric power. Due to the number of variables involved, the task of choosing the optimum driver can be quite involved, and a comparison between the different types of drivers should be done before a final selection is made.

The task of gas compression is to bring gas from a certain suction pressure to a higher discharge pressure by means of mechanical work. The actual compression process is often compared to one of three ideal processes: isothermal, isentropic, and polytropic compression.

Isothermal compression occurs when the temperature is kept constant during the compression process. It is not adiabatic because the heat generated in the compression process has to be removed from the system. The compression process is isentropic or adiabatic reversible if no heat is added to or removed from the gas during compression, and the process is frictionless. With these assumptions, the entropy of the gas does not change during the compression process. The polytropic compression process is like the isentropic cycle reversible, but it is not adiabatic. It can be described as an infinite number of isentropic steps, each interrupted by isobaric heat transfer. This heat addition guarantees that the process will yield the same discharge temperature as the real process.

See also: Enrichment.

Gas Condensate

Gas condensate (sometimes referred to as *condensate*) is a term that has its roots in the natural gas industry and refers to a mixture of low-boiling hydrocarbon liquids obtained by condensation of the vapors of these hydrocarbon constituents, either in the well or as the gas stream emits from the well. In fact, the term can be applied to any gas stream that contains low-boiling hydrocarbon liquids that are obtained by condensation of the vapors of these hydrocarbon constituents.

The condensate is typically pentane (C_5H_{12}) with varying amounts of higher-boiling hydrocarbon derivatives (up to C_8H_{18}), but relatively little methane or ethane; propane (C_3H_8) butane (C_4H_{10}) may be present in condensate by dissolution in the liquids. Depending upon the source of the condensate, benzene (C_6H_6), toluene ($C_6H_5CH_3$), xylene isomers ($CH_3C_6H_4CH_3$), and ethyl benzene ($C_6H_5C_2H_5$) may also be present. Typically, the condensate is a colorless to straw-yellow water-like fluid with an objectionable odor if hydrogen sulfide is present.

The terms *condensate* and *distillate* are often used interchangeably to describe the liquid produced in tanks, but each term stands for a different material. Along with large volumes of gas, some wells produce a water-white or light straw-colored liquid that resembles low-boiling naphtha. The liquid has been called *distillate* because it resembles the products obtained from crude oil in refineries by distilling the volatile components from crude oil.

The knowledge of the phase behavior of gas-condensates is important for the prediction of the behavior of the gas stream, especially during transportation of the gas (when liquid dropout may occur) and during gas clearing. Liquid dropout typically occurs when there is pressure reduction.

See also: Dry Gas, Wet Gas.

Gas-Cooled Reactor

A gas-cooled reactor is a nuclear reactor that uses graphite as a neutron moderator and carbon dioxide as a coolant. Gas-cooled reactors are advanced carbon-dioxide gas cooled reactors – the advanced high-temperature gas-cooled reactors use helium as a coolant and can achieve high fuel utilization rates and operate at high temperatures. They also produce process heat, which can be used for hydrogen production and low-temperature applications such as seawater desalination and district heating.

The gas-cooled fast reactor system is a nuclear reactor design that features a fast neutron spectrum and a closed fuel cycle for efficient conversion of uranium and management of actinides. The reference reactor design is a helium-cooled system operating with an outlet temperature of 850°C (1,560°F) using a direct closed-cycle turbine for high thermal efficiency. Several fuel forms are available for their potential to operate at high temperatures and to ensure an excellent retention of fission products composite ceramic fuel, advanced fuel particles, or ceramic clad elements of actinide compounds. Core configurations are being considered based on pin- or plate-based fuel assemblies or prismatic blocks, which allows for better coolant circulation than traditional fuel assemblies.

The gas-cooled reactor fast reactor operates on fast neutrons; no moderator is needed to slow neutrons down. This means that, apart from nuclear fuel such as uranium, other fuels can be used. The most common is thorium, which absorbs a fast neutron and decays into uranium-233 (^{233}U). This means gas-cooled fast reactor designs have

breeding properties—they can use fuel that is unsuitable in light water reactor designs and breed fuel. Because of these properties, once the initial loading of fuel has been applied into the reactor, the unit can go years without needing fuel. If these reactors are used for breeding, it is economical to remove the fuel and separate the generated fuel for future use.

The reactors are intended for use in nuclear power plants to produce electricity, while at the same time producing (breeding) new nuclear fuel.

See: Nuclear Reactor – Gas-Cooled Reactor.

Gaseous Effluents

Gaseous effluents from refining processes can be valuable products, or they can create a number of environmental problems. During combustion, the combination of hydrocarbon derivatives, nitrogen oxide, and sunlight results in localized low-levels of ozone, or smog. This is particularly evident in large urban areas and especially when air does not circulate well. The use of crude oil products in various vehicles also contributes to the problem in many areas. The primary effects are on the health of those exposed to the ozone, but plant life has been observed to suffer as well.

Refinery gas and other gas streams may contain large amounts of acid gases, such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). Hydrogen chloride (HCl), although not usually considered to be a major pollutant in crude oil refineries, can arise during processing from the presence of brine in crude oil that is incompletely dried. It can also be produced from mineral matter and other inorganic contaminants and is gaining increasing recognition as a pollutant which needs serious attention.

Acid gases corrode refining equipment, harm catalysts, pollute the atmosphere, and prevent the use of hydrocarbon components in petrochemical manufacture. When the amount of hydrogen sulfide is large, it may be removed from a gas stream and converted to sulfur or sulfuric acid. Some gases contain sufficient carbon dioxide to warrant recovery as dry ice, i.e., solid carbon dioxide. And there is now a conscientious effort to mitigate the emission of pollutants from hydrotreating process by careful selection of process parameters and catalysts.

The terms refinery gas and process gas are also often used to include all of the gaseous products and by-products that emanate from a variety of refinery processes. There are also components of the gaseous products that must be removed prior to release of the gases to the atmosphere or prior to use of the gas in another part of the refinery, i.e., as a fuel gas or as a process feedstock.

Crude oil refining produces gas streams often contain substantial amounts of acid gases such as hydrogen sulfide and carbon dioxide. More particularly, hydrogen sulfide arises from the hydrosulfurization of feedstocks that contain organic sulfur:



Crude oil refining involves, with the exception of some of the more viscous crude oils, a primary distillation of the hydrogen mixture, which results in its separation into fractions differing in carbon number, volatility, specific gravity, and other characteristics. The most volatile fraction, that contains most of the gases which are generally dissolved in the crude, is referred to as pipe still gas or pipe still light ends and consists essentially of hydrocarbon gases ranging from methane to butane(s), or sometimes pentane(s).

The gas varies in composition and volume, depending on crude origin and on any additions to the crude made at the loading point. It is not uncommon to re-inject low-boiling hydrocarbon derivatives such as propane and butane into the crude before dispatch by tanker or pipeline. This results in a higher vapor pressure of the crude, but it allows one to increase the quantity of low-boiling products obtained at the refinery. Since light ends in most crude oil markets command a premium, while in the oil field itself propane and butane may have to be re-injected or flared, the practice of spiking crude oil with liquefied petroleum gas is becoming fairly common.

In addition to the gases obtained by distillation of crude oil, more highly volatile products result from the subsequent processing of naphtha and middle distillate to produce gasoline. Hydrogen sulfide is produced in the desulfurization processes involving hydrogen treatment of naphtha, distillate, and residual fuel, and from the

coking or similar thermal treatments of vacuum gas oils and residual fuels. The most common processing step in the production of gasoline is the catalytic reforming of hydrocarbon fractions in the heptane (C_7) to decane (C_{10}) range.

In a series of processes commercialized under the generic name reforming, paraffin and naphthene (cyclic non-aromatic) hydrocarbon derivatives, are altered structurally in the presence of hydrogen and a catalyst into aromatics, or isomerized to more highly branched hydrocarbon derivatives. Catalytic reforming processes thus not only result in the formation of a liquid product of higher octane number, but also produce substantial quantities of gases. The latter are rich in hydrogen, but also contain hydrocarbon derivatives from methane to butanes, with a preponderance of propane ($CH_3CH_2CH_3$), n-butane ($CH_3CH_2CH_2CH_3$), and iso-butane [$(CH_3)_3CH$].

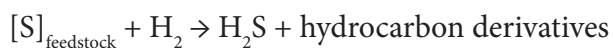
The composition of the process gases varies in accordance with reforming severity and reformer feedstock. All catalytic reforming processes require substantial recycling of a hydrogen stream. Therefore, it is normal to separate reformer gas into a propane ($CH_3CH_2CH_3$) and/or a butane stream [$CH_3CH_2CH_2CH_3$ plus $(CH_3)_3CH$], which becomes part of the refinery liquefied petroleum gas production, and a lower-boiling gas fraction, part of which is recycled. In view of the excess of hydrogen in the gas, all products of catalytic reforming are saturated, and there are usually no olefin gases present in either gas stream.

A second group of refining operations that contributes to gas production is that of the catalytic cracking processes. These consist of fluid-bed catalytic cracking in which high-boiling gas oils are converted into gas, liquefied petroleum gas, catalytic naphtha, fuel oil, and coke by contacting the high-boiling feedstock with the hot catalyst. Both catalytic and thermal cracking processes, the latter being now largely used for the production of chemical raw materials, result in the formation of unsaturated hydrocarbon derivatives, particularly ethylene ($CH_2=CH_2$), but also propylene (propene, $CH_3CH=CH_2$), iso-butylene [iso-butene, $(CH_3)_2C=CH_2$] and the n-butenes ($CH_3CH_2CH=CH_2$, and $CH_3CH=CHCH_3$) in addition to hydrogen (H_2), methane (CH_4) and smaller quantities of ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), and butanes [$CH_3CH_2CH_2CH_3$, $(CH_3)_3CH$]. Diolefins such as butadiene ($CH_2=CHCH=CH_2$) are also present.

Additional gases are produced in refineries with visbreaking and/or coking facilities that are used to process of the heaviest crude fractions. In the visbreaking process, fuel oil is passed through externally fired tubes and undergoes liquid-phase cracking reactions, which result in the formation of lower-boiling fuel oil components. Oil viscosity is thereby reduced, and some gases, mainly hydrogen, methane, and ethane, are formed. Substantial quantities of both gas and carbon are also formed in coking (both delayed coking and fluid coking) in addition to the middle distillate and naphtha. When coking a residual fuel oil or high-boiling gas oil, the feedstock is preheated and contacted with hot carbon (coke) which causes extensive cracking of the feedstock constituents of higher molecular weight to produce lower-molecular-weight products ranging from methane, via liquefied petroleum gas and naphtha, to gas oil and heating oil. Products from coking processes tend to be unsaturated, and olefin components predominate in the tail gases from coking processes.

A further source of refinery gas is hydrocracking, a catalytic high-pressure pyrolysis process in the presence of fresh and recycled hydrogen. The feedstock is again high-boiling gas oil or residual fuel oil, and the process is directed mainly at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again have to be separated into lower-boiling and higher-boiling streams; any surplus recycle gas and the liquefied petroleum gas from the hydrocracking process are both saturated.

Both hydrocracker gases and catalytic reformer gases are commonly used in catalytic desulfurization processes. In the latter, feedstocks ranging from lower-boiling gas oil to vacuum gas oil are passed at pressures of 500 to 1,000 psi (3.5 to 7.0×10^3 kPa) with hydrogen over a hydrofining catalyst. This results mainly in the conversion of organic sulfur compounds to hydrogen sulfide,



The reaction also produces some low-boiling hydrocarbon derivatives by hydrocracking.

Thus refinery streams, while ostensibly being hydrocarbon in nature, may contain large amounts of acid gases such as hydrogen sulfide and carbon dioxide. Most commercial plants employ hydrogenation to convert organic

sulfur compounds into hydrogen sulfide. Hydrogenation is effected by means of recycled hydrogen-containing gases or external hydrogen over a nickel molybdate or cobalt molybdate catalyst.

In summary, refinery process gas, in addition to hydrocarbon derivatives, may contain other contaminants, such as carbon oxides (CO_x , where $x = 1$ and/or 2), sulfur oxides (SO_x , where $x = 2$ and/or 3), as well as ammonia (NH_3), mercaptans (R-SH), and carbonyl sulfide (COS).

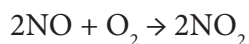
The presence of these impurities may eliminate some of the sweetening processes, since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes not designed to remove (or incapable of removing) large amounts of acid gases whereas they are capable of removing the acid gas impurities to low levels when the acid gases are present only in low-to-medium concentration in the gas.

From an environmental viewpoint, it is not the means by which these gases can be utilized but it is the effects of these gases on the environment when they are introduced into the atmosphere. In addition to the corrosion of equipment of acid gases, the escape into the atmosphere of sulfur-containing gases can eventually lead to the formation of the constituents of acid rain, i.e., the oxides of sulfur (SO_2 and SO_3). Similarly, the nitrogen-containing gases can also lead to nitrous and nitric acids (through the formation of the oxides of nitrogen (NO_x , where $x = 1$ or 2) which are the other major contributors to acid rain. The release of carbon dioxide and hydrocarbon derivatives as constituents of refinery effluents can also influence the behavior and integrity of the ozone layer.

Hydrogen chloride, if produced during refining, quickly picks up moisture in the atmosphere to form droplets of hydrochloric acid and, like sulfur dioxide, is a contributor to acid rain. However, hydrogen chloride may exert severe local effects because, unlike sulfur dioxide, it does not need to participate in any further chemical reaction to become an acid and. Under atmospheric conditions that favor a buildup of stack emissions in the area of a large industrial complex or power plant, the amount of hydrochloric acid in rainwater could be quite high.

Any gas stream is also capable of producing emissions that are detrimental to the environment. For example, constituents such as carbon dioxide (CO), hydrogen sulfide (H_2S), and mercaptans (thiols; R-SH), as well as trace amounts of sundry other emissions can cause considerable harm to the environment. Any removal process must be very precise, since the gas stream may contain only a small quantity of harmful constituents that must be reduced by several orders of magnitude.

It is generally believed (the chemical thermodynamics are favorable) that acidic compounds are formed when sulfur dioxide and nitrogen oxide emissions are released from tall industrial stacks. Gases such as sulfur oxides (usually sulfur dioxide, SO_2) as well as the nitrogen oxides (NO_x) react with the water in the atmosphere to form acids:



Acid rain has a pH less than 5.0 and predominantly consists of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). As a point of reference, in the absence of anthropogenic pollution sources the average pH of rain is approximately 6.0 (slightly acidic; neutral pH = 7.0). In summary, the sulfur dioxide that is produced during a variety of processes will react with oxygen and water in the atmosphere to yield environmentally detrimental sulfuric acid. Similarly, nitrogen oxides will also react to produce nitric acid.

Another acid gas, hydrogen chloride (HCl), although not usually considered to be a major emission, is produced from mineral matter and the brines that often accompany crude oil during production and is gaining increasing

recognition as a contributor to acid rain. However, hydrogen chloride may exert severe local effects because it does not need to participate in any further chemical reaction to become an acid. Under atmospheric conditions that favor a buildup of stack emissions in the areas where hydrogen chloride is produced, the amount of hydrochloric acid in rainwater could be quite high.

In addition to hydrogen sulfide and carbon dioxide, gas may contain other contaminants, such as mercaptans (R-SH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes are also capable of removing the acid gas impurities to low levels when the acid gases are there in low-to-medium concentrations in the gas.

On a regional level the emission of sulfur oxides (SO_x) and nitrogen oxides (NO_x) can also cause the formation of acid species at high altitudes, which eventually precipitate in the form of acid rain, damaging plants, wildlife, and property. At the global level, there is concern that the increased use of hydrocarbon-based fuels will ultimately raise the temperature of the planet (global warming), as carbon dioxide reflects the infrared or thermal emissions from the earth, preventing them from escaping into space (greenhouse effect). Whether or not the potential for global warming becomes real will depend upon how emissions into the atmosphere are handled. There is considerable discussion related to the merits and the de-merits of the global warming theory and the discussion is likely to continue for some time. Be that as it may, the atmosphere can only tolerate pollutants up to a limiting value. And that value needs to be determined. In the meantime, efforts must be made to curtail the use of noxious and foreign (non-indigenous) materials into the air.

Gaseous Fuels

Gaseous fuels are those fuels that are in the gaseous state under ambient conditions (Table G-3). In some circumstances, the definition of gaseous fuels may also include the low-boiling hydrocarbons such as pentane but such fuels are considered to be liquid fuels.

Table G-3 General properties and description of gaseous fuels.

	Molecular weight	Specific gravity	Boiling	Ignition
			Point, °F	Temperature, °F
Methane	16.0	0.553	-258.7	900-1170
Ethane	30.1	0.572	-127.5	959
Ethylene	28.0		-154.7	914
Propane	44.1		-43.8	842
Propylene	42.1		-53.9	856
n-Butane	58.1	0.601	31.1	761
iso-Butane	58.1		10.9	864
n-Butene	56.1	0.595	21.2	829
iso-Butene	56.1		19.6	869

The terminology used to describe gaseous fuels is variable (Table G-4), and sincere efforts must be made to accurately identify the gaseous fuel on the basis of type and composition.

Table G-4 Common terminology used to describe gases fuels.

Acid gas	A gas containing hydrogen sulfide (H_2S) and/or carbon dioxide (CO_2).
Biogas	A medium Btu gas containing methane and carbon dioxide, resulting from the action of microorganisms on organic materials such as a landfill.
Blue gas	A mixture consisting chiefly of carbon monoxide (CO) and hydrogen (H_2) typically formed by action of steam on hot coal or coke.
Carbon monoxide	A colorless, odorless, very toxic gas formed by incomplete combustion of carbon, as in water gas or producer gas production.
Carbureted blue gas	See Water gas.
Carbureted gas	Gas that has been passed been in contact with a liquid fuel and thereby mixing the air/gas and fuel.
Coal gas	The mixture of volatile products (mainly hydrogen, methane, carbon monoxide, and nitrogen) remaining after removal of water and tar, obtained from carbonization of coal, having a heat content on the order of 400-600 Btu/ft ³ .
Coke-oven gas	A medium-Btu gas, typically 550 Btu/ft ³ , produced as a by-product in the manufacture of coke by heating coal at moderate temperatures.
Destructive distillation	The process of pyrolysis conducted in a distillation apparatus to allow the volatile products to be collected. Sometimes referred to as cracking distillation.
Flue gas	The gas removed from a process (or process reactor or boiler) by a flue or chimney.
Gasification	A partial oxidation process that converts carbonaceous materials into a gaseous mixture of carbon monoxide and hydrogen (also known as synthesis gas) by reacting the raw material at high temperatures with controlled amounts of oxygen and/or steam.
High-Btu gas	A nitrogen-rich gas with a heat content of >800 Btu/ft ³ produced in gasification processes.
Landfill gas	Gas produced by the decay of organic matter in a landfill; often referred to as biogas.
Liquefied petroleum gas	Also known as LPG; a mixture of liquefied propane and butane.
Low-Btu gas	A nitrogen-rich gas with a heat content of 550 Btu/ft ³ produced in gasification processes using air as the source of the oxidant (oxygen); the air-blown form of producer gas.
Manufactured gas	A gas obtained by destructive distillation of coal, or by the thermal decomposition of crude oil, or by the reaction of steam passing through a bed of heated coal or coke. Examples are coal gases, coke oven gases, producer gas, blast furnace gas, blue (water) gas, and carbureted water gas. Btu content varies widely.
Medium-Btu gas	A gas with a heat content on the order of 100 to 200 Btu/ft ³ produced in gasification processes.
Producer gas	A gas mixture containing carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and nitrogen (N_2). In some countries, producer gas is a generic term referring to wood gas or town gas or syngas. The heat content may be on the order of 110-160 Btu/ft ³ (air combustion) or 400-500 Btu/ft ³ (oxygen combustion). The gas may be used to power gas turbines which are suited to fuels of low calorific value.
Pyrolysis	The thermal decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam.
Refinery gas	Non-condensable gas collected in a petroleum refinery.
Stack gas	The product gas evolved during complete combustion of a fuel.
Sweetened gas	Gas from which acid (sour) gases such as hydrogen sulfide (and in some cases) carbon dioxide has been removed.
Synthetic natural gas	A pipeline-quality gas that is interchangeable with natural gas (mainly methane); also referred to as substitute natural gas.
Synthesis gas	A gas mixture that contains varying amounts of carbon monoxide (CO) and hydrogen (H_2) generated by the gasification of a carbonaceous material to a gaseous product.

(Continued)

Table G-4 Common terminology used to describe gases fuels. (*Continued*)

Tail gas	Residual gas leaving a process and not always required for further processing.
Town gas	Contains hydrogen (H ₂), carbon monoxide (CO), carbon dioxide (CO ₂), methane (CH ₄), nitrogen (N ₂), and volatile hydrocarbon derivatives. Produced by blowing air and steam over an incandescent fuel bed, usually of coke or coal; typically has a heat content on the order of 600 Btu/ft ³ .
Water gas	A mixture of carbon monoxide (CO) and hydrogen (H ₂) produced by passing steam over red-hot coke using the endothermic reaction $C + H_2O \rightarrow CO + H_2$. This product had a lower calorific value than coal gas, so the gas is often passed through a heated retort into which oil was sprayed to produce carbureted water gas; sometimes referred to as carbureted blue gas.
Wood gas	The product of thermal gasification of woody biomass (such as wood chips, wood waste, and sawdust) in a gasifier or wood gas generator. It is the result of a high temperature reaction (>700°C, 1,290°F) where the feedstock reacts with steam or a limited amount of air producing carbon monoxide (CO), carbon dioxide (CO ₂), hydrogen (H ₂), and methane (CH ₄). After the gas is filtered, purified (scrubbed), and used to power gas turbines.

Biogas is a clean and renewable form of energy, and the most important biogas components are methane (CH₄), carbon dioxide (CO₂), and sulfuric components (H₂S). The gas generally composes of methane (55 to 65%), carbon dioxide (35 to 45%), nitrogen (0 to 3%), hydrogen (0 to 1%), and hydrogen sulfide (0 to 1%).

Biogas could very well substitute for conventional sources of energy (i.e., fossil fuels) which are causing ecological–environmental problems and at the same time, depleting at a faster rate. Due to its elevated methane content, resultant of the organic degradation in the absence of molecular oxygen, biogas is an attractive source of energy. The physical, chemical, and biological characteristics of the manure are related to diet composition, which can influence the biogas composition. The biogas composition is an essential parameter because it allows identifying the appropriate purification system, which aims to remove sulfuric gases and decrease the water volume, contributing to improve the combustion fuel conditions.

Biogas production has usually been applied for waste treatment, mainly sewage sludge, agricultural waste (manure), and industrial organic waste streams. The primary source, which delivers the necessary microorganisms for biomass biodegradation and as well, one of the largest single sources of biomass from food/feed industry, is manure from animal production, mainly from cows and pig farms.

Currently, biogas production is mainly based on the anaerobic digestion of single energy crops. Maize, sunflower, grass, and Sudan grass are the most commonly used energy crops. In the future, biogas production from energy crops will increase and requires to be based on a wide range of energy crops that are grown in versatile, sustainable crop rotations.

A specific source of biogas is landfills. In a typical landfill, the continuous deposition of solid waste results in high densities and the organic content of the solid waste undergoes microbial decomposition. The production of methane-rich landfill gas from landfill sites makes a significant contribution to atmospheric methane emissions. In many situations, the collection of landfill gas and production of electricity by converting this gas in gas engines is profitable and the application of such systems has become widespread. The benefits are obvious: useful energy carriers are produced from gas that would otherwise contribute to a build-up of methane in the atmosphere, which has stronger greenhouse gas impact than the carbon dioxide emitted from the power plant. This makes landfill gas utilization in general an attractive greenhouse gas mitigation option, which is being increasingly deployed in world regions.

Generally, biogas is most commonly produced by using animal manure mixed with water, which is stirred and warned inside an airtight container, known as a digester. The most important biogas components are methane, carbon dioxide, and sulfuric components. The gas is generally composed of methane (55 to 65%), carbon dioxide (35 to 45%), nitrogen (0 to 3%), hydrogen (0 to 1%), and hydrogen sulfide (0 to 1%).

Anaerobic processes could either occur naturally or in a controlled environment such as a biogas plant. Organic waste such as livestock manure and various types of bacteria are put in an airtight container called digester so the process could occur. In the complex process of anaerobic digestion, hydrolysis/acidification and methanogenesis are considered as rate-limiting steps.

Most biomass materials are easier to gasify than coal because they are more reactive with higher ignition stability. This characteristic also makes them easier to process thermochemically into higher-value fuels such as methanol or hydrogen. Ash content is typically lower than for most coals, and sulfur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a

soil amendment to help replenish nutrients removed by harvest. A few biomass feedstocks stand out for their peculiar properties, such as high silicon or alkali metal contents – these may require special precautions for harvesting, processing, and combustion equipment. Note also that mineral content can vary as a function of soil type and the timing of feedstock harvest. In contrast to their fairly uniform physical properties, biomass fuels are rather heterogeneous with respect to their chemical elemental composition.

A number of processes allow biomass to be transformed into gaseous fuels such as methane or hydrogen. One pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Problems are intermittent production, low efficiency, and difficulty in constructing hydrogen collection and transport channels of low cost. A second pathway uses plant material such as agricultural residues in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment, but often with the energy produced only for onsite use, which often implies less than maximum energy yields. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. In addition to biogas, there is also the possibility of using the solid by-product as a biofuel.

The technologies for gas production from biomass include processes such as (i) fermentation, (ii) gasification, and (iii) direct biophotolysis.

See also: Aerobic Digestion, Anaerobic Digestion, Biofuels, Biomass, Natural Gas.

Gaseous Fuels from Waste

There are two ways of producing gaseous fuel from waste, and these are (i) gasification of the waste at high temperatures by partial oxidation and then conversion of materials containing carbon into synthesis gas (mainly hydrogen and carbon monoxide) and (ii) production of biogas, mainly methane, by the anaerobic digestion of waste.

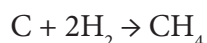
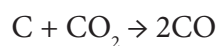
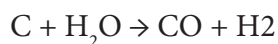
Gasification is the general term used for processes where heat is used to transform a feedstock, usually a solid feedstock such as coal or biomass applicable to the conversion of any solid carbonaceous waste to a clean burning gaseous fuel. Whether starting with coffee grounds, municipal trash, or junk tires, the end product is a flexible gaseous fuel, and with the relevant process modifications, production of liquid and solid fuels is also possible.

Biochemical conversion options can be divided into digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol). With respect to thermochemical conversion options, a distinction can be made between combustion, gasification, and pyrolysis.

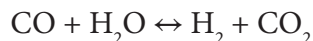
Anaerobic digestion is a process whereby organic waste is broken down in a controlled, oxygen-free environment by bacteria naturally occurring in the waste material. Methane rich biogas is produced, thus facilitating renewable energy generation. As a result, materials that are currently going to landfill can be utilized; natural methane emissions are reduced, and conventional generation with its associated carbon emissions is displaced. The residual nutrient-rich liquor and digestate are suitable for use as fertilizer on the farmland surrounding such a plant, reducing the need for artificial fertilizer. In summary, anaerobic digestion is a form of composting.

While solid wastes were somewhat in focus for the gasification and pyrolysis activities, around 1970, biomass gasification took over the central role when the oil prices went up after 1973.

The principle behind waste gasification and the production of gaseous fuels is that that waste contains carbon, and it is this carbon that is converted to gaseous products via the usual gasification chemistry. Thus, when fuel is fed to a gasifier, water and volatile matter are released fast and a char residue is left to react further. The char gasification is what mainly controls the conversion achieved in the process. From solid carbon, product gas is formed according to the following main reactions:



In addition to the reactions of solid carbon, the most important reaction is the water-gas-shift reaction, which takes place in the gas phase:



The product gas generally contains large amounts of hydrogen and carbon monoxide and a small amount of methane, as well as carbon dioxide and steam, and in air gasification nitrogen. In addition, a significant amount of other organic components in the gas, known as tar, is formed. Tar formation can also be anticipated to form in the gasification or pyrolysis of any complex carbonaceous material.

Biomass-based fuels (and many components of domestic and industrial waste can be included in this category) are non-fossil fuels. Vegetative biomass can be classified into the categories woody, herbaceous, agricultural by-products, energy crops, and black liquor (a by-product of the forest industry. Because of the high concentration of organic materials in industrial waste and in domestic waste (including discarded food), many constituents of waste are actually biomass. But the issues arise from the other constituents of the waste that make the waste truly heterogeneous and, in many cases, of indeterminate composition.

See also: Gaseous Fuels (Volume 3: Coal), Gasification, Gasification (Volume 3: Coal).

Gaseous Fuels from Waste – Reactors

Most of the reactors were of the fixed-bed type (updraft or downdraft) and are considered to be adequate processes for local use in terms of the alternate, i.e., landfilling the waste. However, whether wastes should be handled locally or in a large scale, centralized units is another issue that is still under debate.

Thus, a process for waste gasification must be chosen to reflect the character of the waste relation to the main questions in this report as stated in the introduction. However, few of the original processes touted as potential methods for waste gasification may not be in current commercial use and reference must be made to gasification processes (for coal) that are in current commercial use.

Processes proposed for waste gasification should include a separation step. Feedstock homogeneity is a pre-requisite for many gasifiers, and feedstock heterogeneity and process scale-up can lead to a number of mechanical problems, shut-downs, sintering, and hot spots leading to corrosion and eventual failure of the reactor wall. In addition, the heterogeneity of the non-carbon constituents of the waste and their influence on the process chemistry are often difficult to estimate.

Most of these process efforts included use of a fixed-bed reactor on the basis of applicability of coal gasification is also applicable to waste. The most common equipment was a shaft reactor with a bottom temperature of approximately 1,000°C (1,830°F) leading to transport problems within the reactor bed and in the shaft to the ash outlet, such as ash sintering. The character of coal ash and its effect on gasification is well understood. The effect of ash from waste is not yet fully understood and requires extra effort before a suitable reactor can be proposed for waste gasification.

Finally, most of the systems proposed for waste gasification produced tar or a mixture of tar and gas and very few of the processes included gas cleaning. Thus, the tar-rich gas caused problems on the gas side as well as tar condensation in the pipes to the combustor. On the other hand, waste that contained metals, glass, and inorganic materials which sinter and melt at higher temperatures also caused reactor problems.

Overall, the heterogeneous composition of domestic and industrial waste has not been beneficial in terms of the gasification of the waste. Recycling programs in which the first is first separated into various components may be a necessary prelude to waste gasification. With energy prices (crude oil and natural gas) currently at an all-time high, and threatening to continue at high levels for the foreseeable future, the time is now for development of waste gasification processes.

See also: Gaseous Fuels, Gasification, Liquid Fuels, Solid Fuels.

Gaseous Fuels from Wood

Wood can be used to make both liquid and gaseous fuels. When wood is heated in the absence of air, or with a reduced air supply, it is possible to produce a liquid fuel which can be used in a similar way to conventional oil fuels.

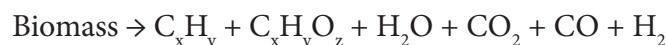
It can be used to run internal combustion engines in vehicles or generators. The gas produced from wood is a mixture of hydrogen and carbon monoxide which can be used in internal combustion engines or in gas turbines which can be used to power generators. Although the liquid fuels are rarely produced from wood at present, wood gas is important in other countries for producing electricity in more remote areas.

Thus, gasification technology is an attractive route for the production of fuel gases from biomass. By gasification, solid biomass is converted into a combustible gas mixture normally called producer gas consisting primarily of hydrogen (H_2) and carbon monoxide (CO), with lesser amounts of carbon dioxide (CO_2), water (H_2O), methane (CH_4), and higher hydrocarbons (C_xH_y), as well as nitrogen (N_2) and particulates.

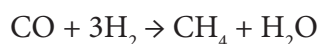
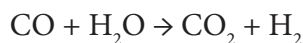
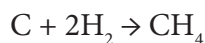
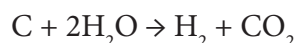
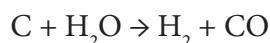
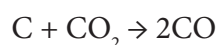
The gasification is carried out at elevated temperatures, 500°C and 1,500°C and at atmospheric or elevated pressures. The process involves conversion of biomass, which is carried out in absence of air or with less air than the stoichiometric requirement of air for complete combustion. Partial combustion produces carbon monoxide as well as hydrogen which are both combustible gases. Solid biomass fuels, which are usually inconvenient and have low efficiency of utilization, can be converted into gaseous fuel. The energy in producer gas is 70% to 80% of the energy originally stored in the biomass. The producer gas can serve in different ways: it can be burned directly to produce heat or used as a fuel for gas engines and gas turbines to generate electricity; in addition, it can also be used as a feedstock (syngas) in the production of chemicals, e.g., methanol. The diversified applications of the producer gas make the gasification technology attractive.

A variety of biomass gasifiers has been developed and can be grouped into four major classes which are (i) the fixed-bed updraft or countercurrent gasifier, (ii) the fixed-bed downdraft or co-current gasifier, (iii) the bubbling fluidized-bed gasifier, and (iv) the circulating fluidized bed gasifier. Differentiation is based on the means of supporting the biomass in the reactor vessel, the direction of flow of both the biomass and oxidant, and the way heat is supplied to the reactor. The processes occurring in any gasifier include drying, pyrolysis, reduction, and oxidation. The unique feature of the updraft gasifier is the sequential occurrence of these processes: they are separated spatially and therefore temporally.

Using the updraft gasifier as an example, biomass and air are fed in an opposite direction. In the highest zone, biomass is heated up and releases its moisture. In the pyrolysis zone, biomass undergoes a further increase in temperature and decomposes into hydrocarbons, gas products, and char in the temperature range of 150°C to 500°C. The major reactions are:

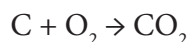


The hydrocarbon fraction consists of methane to high boiling tar. The composition of this fraction can be influenced by many parameters, such as particle size of the biomass, temperature, pressure, heating rate, residence time, and catalysts. The operative reactions are:



The composition of the producer gases varies widely with the properties of the biomass, the gasifying agent, and the process conditions. Depending on the nature of the raw solid feedstock and the process conditions, the char formed from pyrolysis contains 20% to 60% of the energy input. Therefore, the gasification of char is an important step for the complete conversion of the solid biomass into gaseous products and for an efficient utilization of the energy in the biomass.

The producer gases from the reduction zone rise beyond the reduction zone. When they come into contact with the cooler biomass, the temperature drops down and the aforementioned reactions are frozen. The unreacted char further undergoes the oxidation with air in the lowest zone:



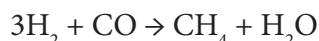
As a result, ash is left at the bottom of the reactor. The produced carbon dioxide flows upward and is involved in the reactions in the reduction zone. The heat released in the oxidation zone drives both the reduction and pyrolysis processes.

See also: Gaseous Fuels, Gasification.

Gaseous Fuels – High Btu Gas

High Btu gas (high heat-content gas) is essentially pure methane and often referred to as synthetic natural gas or substitute natural gas (SNG). However, to qualify as substitute natural gas, a product must contain at least 95% v/v methane, giving an energy content (heat content) of synthetic natural gas on the order of 980 to 1,080 Btu/ft³.

The commonly accepted approach to the synthesis of high heat-content gas is the catalytic reaction of hydrogen and carbon monoxide:



To avoid catalyst poisoning, the feed gases for this reaction must be quite pure and, therefore, impurities in the product are rare. The large quantities of water produced are removed by condensation and recirculated as very pure water through the gasification system. The hydrogen is usually present in slight excess to ensure that the toxic carbon monoxide is reacted; this small quantity of hydrogen will lower the heat content to a small degree.

The carbon monoxide/hydrogen reaction is somewhat inefficient as a means of producing methane because the reaction liberates large quantities of heat. In addition, the methanation catalyst is troublesome and prone to poisoning by sulfur compounds and the decomposition of metals can destroy the catalyst. Hydrogasification may be thus employed to minimize the need for methanation:



The product of hydrogasification is far from pure methane, and additional methanation is required after hydrogen sulfide and other impurities are removed.

See also: Gaseous Fuels.

Gas Fuels – Low Btu Gas

Low Btu gas (low heat content gas) is produced during the process by oxidation of the feedstock with air; the oxygen is not separated from the air, and, as a result, the gas product invariably has a low heat-content (150 to 300 Btu/ft³). Low heat-content gas contains several components, four of which are always major components present at levels of at least several percent; a fifth component, methane, is marginally a major component.

The nitrogen content of low heat-content gas ranges from somewhat less than 33% v/v to slightly more than 50% v/v and cannot be removed by any reasonable means; the presence of nitrogen at these levels makes the product gas *low heat-content* by definition. The nitrogen also strongly limits the applicability of the gas to chemical synthesis. Two other noncombustible components (water, H₂O, and carbon dioxide, CO₂) further lower the heating value of the gas; water can be removed by condensation and carbon dioxide by relatively straightforward chemical means.

The two major combustible components are hydrogen and carbon monoxide; the H₂/CO ratio varies from approximately 2:3 to approximately 3:2. Methane may also make an appreciable contribution to the heat content of the gas. Of the minor components, hydrogen sulfide is the most significant and the amount produced is, in fact, proportional to the sulfur content of the feed coal. Any hydrogen sulfide present must be removed by one, or more, of several procedures.

Low heat-content gas is of interest to industry as a fuel gas or even, on occasion, as a raw material from which ammonia, methanol, and other compounds may be synthesized.

See also: Gaseous Fuels.

Gaseous Fuels – Medium Btu Gas

Medium heat-content gas (medium heat-content gas) has a heating value in the range 300 to 550 Btu/ft³, and the composition is much like that of low heat-content gas, except that there is virtually no nitrogen. The primary combustible gases in medium heat-content gas are hydrogen and carbon monoxide. Medium heat-content gas is considerably more versatile than low heat-content gas; like low heat-content gas, medium heat-content gas may be used directly as a fuel to raise steam, or used through a combined power cycle to drive a gas turbine, with the hot exhaust gases employed to raise steam, but medium heat-content gas is especially amenable to synthesize methane (by methanation), higher hydrocarbon derivatives (by Fischer-Tropsch synthesis), methanol, and a variety of synthetic chemicals.

The reactions used to produce medium heat-content gas are the same as those employed for low heat-content gas synthesis, the major difference being the application of a nitrogen barrier (such as the use of pure oxygen) to keep diluent nitrogen out of the system.

In medium heat-content gas, the H₂/CO ratio varies from 2:3 C to 3:1 and the increased heating value correlates with higher methane and hydrogen contents as well as with lower carbon dioxide contents. Furthermore, the very nature of the gasification process used to produce the medium heat-content gas has a marked effect upon the ease of subsequent processing. For example, the CO₂-acceptor product is quite amenable to use for methane production because it has (i) the desired H₂/CO ratio just exceeding 3:1, (ii) an initially high methane content, and (iii) relatively low water and carbon dioxide contents. Other gases may require appreciable shift reaction and removal of large quantities of water and carbon dioxide prior to methanation.

See also: Gaseous Fuels.

Gases and Naphtha

Methane is the main hydrocarbon component of crude oil gases with lesser amounts of ethane, propane, butane, isobutane, and some C₄⁺ hydrocarbon derivatives. Other gases, such as hydrogen, carbon dioxide, hydrogen sulfide, and carbonyl sulfide, are also present.

Saturated constituents with lesser amounts of mono- and di-aromatics dominate the naphtha fraction. While naphtha covers the boiling range of gasoline, most of the raw crude oil naphtha molecules have low octane number. However, most raw naphtha is processed further and combined with other process naphtha and additives to formulate commercial gasoline.

Within the saturated constituents in crude oil gases and naphtha, every possible paraffin from methane (CH₄) hydrocarbon to n-decane (n-C₁₀H₂₂, normal decane) is present. Depending upon the source, one of these low boiling paraffins may be the most abundant compound in a crude oil reaching several percent. The iso-paraffins begin at C₄ with isobutane as the only isomer of n-butane. The number of isomers grows rapidly with carbon number, and there may be increased difficulty in dealing with multiple isomers during analysis.

In addition to aliphatic molecules, the saturated constituents consist of cycloalkanes (naphthenes) with predominantly five- or six-carbon rings. Methyl derivatives of cyclopentane and cyclohexane, which are commonly found at higher levels than the parent unsubstituted structures, may be present. Fused ring dicycloalkane derivatives such as cis-decahydronaphthalene (cis-decalin) and trans-decahydronaphthalene (trans-decalin) and hexahydro-indan are also common, but bicyclic naphthenes separated by a single bond, such as cyclohexyl cyclohexane, are not.

The numerous aromatic constituents in crude oil naphtha begin with benzene, but its C₁ to C₃ alkylated derivatives are also present. Each of the alkyl benzene homologues through the twenty isomeric C₄ alkyl benzenes have been isolated from crude oil along with various C₅-derivatives. Benzene derivatives having fused cycloparaffin rings (naphthoaromatic derivatives) such as indane and tetralin have been isolated along with a number of their methyl derivatives. Naphthalene is included in this fraction, while the 1- and 2-methyl naphthalenes and higher homologues of fused two ring aromatics appear in the mid-distillate fraction.

Sulfur-containing compounds are the only heteroatom compounds to be found in this fraction. Usually, the total amount of the sulfur in this fraction accounts for less than 1% of the total sulfur in the crude oil. In naphtha from high-sulfur (sour) crude oil, 50 to 70% of the sulfur may be in the form of mercaptans (thiols). Over 40 individual thiols have been identified, including all the isomeric C_1 to C_6 compounds plus some C_7 and C_8 isomers plus thiophenol. In naphtha from low-sulfur (sweet) crude oil, the sulfur is distributed between sulfides (thioethers) and thiophenes. In these cases, the sulfides may be in the form of both linear (alkyl sulfides) and five- or six-ring cyclic (thiacyclane) structures. The sulfur structure distribution tends to follow the distribution hydrocarbon derivatives such as naphthenic oils with a high content of cycloalkane derivatives tend to have a high thiacyclane content. Typical alkyl thiophene derivatives in naphtha have multiple short side chains or exist as naphthothiophene derivatives. Methyl and ethyl disulfides have been confirmed to be present in some crude oils in analyses that minimized their possible formation by oxidative coupling of thiol (mercaptan) derivatives.

See also: Gaseous Fuels, Liquid Fuels.

Gaseous Hydrocarbons – General Properties

The number of carbon atoms in a member of the paraffin series determines whether the hydrocarbon will exist as a gas, a liquid, or a solid under standard conditions of temperature and pressure (STP' 60°F, 760 mm Hg) (Table G-5). Methane (CH_4) is a gas under all naturally occurring temperature and pressure conditions. Ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and its isomers are gaseous under standard surface conditions (Table G-5) but may exist in either gaseous or liquid phase under the elevated temperature and pressure conditions found in subsurface reservoirs. On the other hand, members of the paraffin series with between 5 and 17 carbon atoms in their molecular structures (such as pentane, C_5H_{12} , hexane, C_6H_{14} , heptane, C_7H_{16} , octane, C_8H_{18}) are liquid under standard surface conditions and most temperature and pressure conditions encountered in subsurface reservoirs. Members of the paraffin series with more than 17 carbon atoms are solid under most naturally occurring temperatures and pressures and, as a mixture, are often referred to as paraffin wax.

Table G-5 Properties of gaseous (C_1 - C_4) paraffin hydrocarbons.

Gas	Molecular weight	Boiling point 1 atm, °C (OF)	Density at 60°F g/liter	Density Relative to air = 1
Methane	16.043	-161.5 (-258.7)	0.6786	0.5547
Ethylene	28.054	-103.7 (-154.7)	1.1949	0.9768
Ethane	30.068	-88.6 (-127.5)	1.2795	1.046
Propylene	42.081	-47.7 (-53.9)	1.8052	1.4757
Propane	44.097	-42.1 (-43.8)	1.8917	1.5464
1,2- Butadiene	54.088	10.9 (51.6)	2.3451	1.9172
1,3-Butadiene	54.088	-4.4 (24.1)	2.3491	1.9203
1-Butene	56.108	-6.3 (20.7)	2.4442	1.9981
cis-2-Butene	56.108	3.7 (38.7)	2.4543	2.0063
trans-2-Butene	56.108	0.9 (33.6)	2.4543	2.0063
iso-Butene	56.104	-6.9 (19.6)	2.4442	1.9981
n-Butane	58.124	-5.4 (31.1)	2.532	2.0698
iso-Butane	58.124	-11.7 (10.9)	2.5268	2.0656

See also: Alkane, Alkenes.

Gaseous Pollutants

The atmosphere of the Earth is a mixture primarily of the gases nitrogen and oxygen, totaling 99%; nearly 1% water; and small amounts of other gases and substances, some of which are chemically reactive. With the exception of oxygen, nitrogen, water, and the inert gases, all constituents of air may be a source of concern owing either to their potential health effects on humans, animals, and plants, or to their influence on the climate.

The gaseous pollutants are carbon monoxide, nitrogen oxides, volatile organic compounds, and sulfur dioxide. These are reactive gases that in the presence of sunlight contribute to the formation of ground level ozone, smog, and acid rain.

The non-gaseous particulate matter consists of metals and substances such as pollen, dust, and larger particles such as soot from wood fires or diesel fuel ignition.

The greenhouse gases are water vapor, carbon dioxide, methane, nitrous oxide, and a host of engineered chemicals, such as chlorofluorocarbons. These gases regulate the temperature of the Earth, and, when the natural balance of the atmosphere is disturbed particularly by an increase or decrease in the greenhouse gases, the climate of the Earth could be affected.

Most greenhouse gases occur naturally, but concentrations of carbon dioxide and other greenhouse gases in the atmosphere of the Earth have been increasing since the Industrial Revolution with the increased combustion of fossil fuels and increased agricultural operations. The greenhouse effect happens because of certain naturally occurring substances in the atmosphere.

Carbon dioxide is a colorless gas that is a by-product of the combustion of organic matter which comprises less than 0.04% v/v of the atmosphere of the Earth, most of which was put there by volcanic activity early in the life of the Earth. Currently, human activities are pumping huge amounts of carbon dioxide into the atmosphere, resulting in an overall increase in carbon dioxide concentrations. These increased concentrations are considered the primary factor in global warming because carbon dioxide absorbs infrared radiation. Most of the energy that escapes the atmosphere of the Earth is in this form, so extra carbon dioxide means more energy absorption and an overall increase in the temperature of the Earth.

Nitrous oxide (NO_2) is another important greenhouse gas. Although the amounts being released by human activities are not as great as the amounts of carbon dioxide, nitrous oxide absorbs much more energy than carbon dioxide (approximately 270 times as much). For this reason, efforts to curb greenhouse gas emissions have focused on nitrous oxide as well. Methane is a combustible gas, and it is the main component of natural gas and also occurs naturally through the decomposition of organic material and is often encountered in the form of swamp gas. Methane acts much like carbon dioxide in the atmosphere, absorbing infrared energy and keeping heat energy on Earth.

See also: Atmosphere, Pollutant.

Gaseous Pollutants – Control

Any gas that is present in the air in a concentration that causes some deleterious effect is considered a gaseous pollutant. However, there are several substances that, by virtue of their massive rates of emission and harmful effects, are considered the most significant pollutants. Four major primary gaseous air pollutants (so called because they are exited from the exhaust pipe into the atmosphere) include sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and carbon monoxide (CO). Basically, these four pollutants are emitted during fossil fuel combustion both from stationary and mobile sources, but each can be emitted from non-combustion processes as well such as SO_x from smelting furnaces, escape of organic vapors from oil tanks, and NO_x from agricultural operations.

There are several methods that can be used to accomplish control of the emissions of gaseous pollutants. However, the method selected and employed must be chosen according to the types of pollutants. Thus, air pollution control devices are a series of devices that work to prevent a variety of different pollutants (both gaseous and solid) from entering the atmosphere primarily out of industrial smokestacks. These control devices can be separated into two broad categories which are (i) devices that control the amount of particulate matter escaping into the environment

and (ii) devices that control emission of acid gases. It is important to understand that the extraction methods for each specific type of pollutant can differ, and the devices presented below (in alphabetical order rather than by preference or use) have been shown to be effective in the past with the overall levels of emissions for many pollutants dropping with the implementation of these control devices.

Gas Control

More intense chemical methods of separation are generally required to separate polluting gases from the flue gas. However, this extraction is important as many acidic gases in flue gas contribute to acid rain. Below are some of the basic ways that gases can be extracted.

Carbon Capture

Carbon dioxide can theoretically also be captured and stored underground or in forests and oceans to prevent it from entering the atmosphere. Carbon capture and storage refers to the process of capturing this carbon dioxide and storing it below ground, pumping it into geologic layers.

Incineration

Incineration is used to convert emissions of volatile organic compounds into carbon dioxide and water. The incineration generally takes place in a specialized piece of equipment known as an afterburner, which is built to create the conditions necessary for complete combustion (such as sufficient burn time and a high temperature). In addition, the incinerated gas must be mixed to ensure complete combustion.

Scrubbers

Scrubbers are a type of system that is used to remove harmful materials from industrial exhaust gases before they are released into the environment. These pollutants are generally gaseous, and when scrubbers are used to specifically remove sulfur oxides, it is referred to as flue gas desulfurization. There are two main types of scrubbers: (i) wet scrubbers and (ii) dry scrubbers. The main difference is in the type of material used to remove the gases. By removing acidic gases from the exhaust before it is released into the sky, scrubbers help prevent the formation of acid rain.

Particulate Matter

Specific processes are used to remove particulate matter from flue gases. Much of this separation uses physical means of separation and not chemical separation techniques simply because particulate matter is large enough to be «caught» in this manner. Below are some of the basic ways that particulate matter can be extracted.

Cyclone Separators

A cyclone separator is a separation device that uses the principle of inertia to remove particulate matter from flue gases.^[3] In these separators, dirty flue gas enters a chamber containing a vortex, similar to a tornado. Because of the difference in inertia of gas particles and larger particulate matter, the gas particles move up the cylinder while larger particles hit the inside wall and drop down. This separates the particulate matter from the flue gas, leaving cleaned gas stream.

Electrostatic Precipitators

An electrostatic precipitator is a type of filter that uses static electricity to remove soot and ash from gas streams before the gas enters the atmosphere. Unburned particles of carbon in the gas stream are removed from the stream by using static electricity in the precipitators.

Fabric Filters

Fabric filters can be used to remove dust from flue gases. In some gases, they can also remove acidic gases if they utilize basic compounds. This method simply uses a fabric – generally, felt is used as a woven cloth would allow dust to make its way through which is placed so that flue gasses must pass through it before exiting into the atmosphere. When the gas passes through, dust particles are trapped in the cloth.

See also: Gas Cleaning, Acid Rain.

Gasification

Gasification is a chemical or thermal process used to convert carbonaceous material (such as coal, crude oil, and biomass) into gaseous components such as carbon monoxide and hydrogen.

Gasification, among the several thermochemical conversion processes, possesses great potential in the advanced utilization of biomass and wastes as a source for energy and material.

In the gasification process, biomass and solid waste are transformed into gas, which can be burned directly as fuel or used as a raw material for synthesis gas or hydrogen production. Considerable environmental importance rests upon the development of highly efficient power cycles and on the production of liquid biofuels and hydrogen from these renewable energy sources. Even though gasification technologies have recently been successfully demonstrated, they continue to be expensive relative to energy production based on fossil fuels. Strong drivers to develop and commercialize biomass and waste gasification exist, however, in face of the urgent need to increase the rates of biomass use and waste recycling and to improve the efficiency of their use in electricity production.

The primary objective of biomass gasification is to convert as much of the feed material as possible to a gaseous product. A secondary objective might be to increase the H_2/CO ratio of the gas over that obtained in pyrolysis so as to facilitate downstream upgrading. This latter objective can be effectively achieved using a subsequent gas shift step. Apart from upgrading to synthetic natural gas, liquid products can be produced by the Fischer-Tropsch synthesis.

The feedstock entering a gasifier is first dried by rising hot gases. Further heating results in the devolatilization and pyrolysis reactions discussed in the previous section. In the next stage, temperatures are sufficiently high for the gasification reactions to proceed.

The raw gas produced on gasification of a carbonaceous feedstock has a low-to-medium-calorific value, depending on whether air or oxygen is used as the oxidant in directly heated gasifiers. The product from indirectly heated gasifiers, in which an inert material is typically used to transfer the heat from an external source, is generally a medium-heat content gas. The energy in these gases could theoretically be utilized directly, for example, by generation of electricity, either by raising steam in a boiler or by combustion in a gas turbine.

The gases produced on gasification do not satisfy the clean fuel criteria, and so further processing is necessary. Removal of pollutant gases such as ammonia and hydrogen sulfide, and inert gases such as carbon dioxide, is an obvious requirement. Gas purification processes do not involve reactions of the active gas components.

Gasification with air results in a low-heat content gas that can be used for combined cycle electricity generation. Increased efficiencies attained with combined cycle systems gasifying conventional fossil fuels arise in part from the more effective pollution control techniques that may be used. In the case of biomass, sulfur concentrations are low, so its direct combustion does not require an attendant energy-consuming flue gas desulfurization step. Other factors including nitrogen oxide emissions, the inherent greater efficiency of gas turbines, and the limited scale of operations, will determine whether or not combined cycle generation with biomass will be more viable than conventional steam-electric generation.

If heat or steam is the desired product, then again air gasification appears to offer little advantage over direct combustion as far as pollution control is concerned. It is possible that air gasification may prove useful as a means of providing a substitute fuel for existing gas-fired boilers.

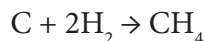
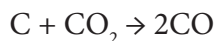
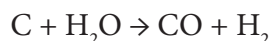
A gasifier supplying fuel to an adjacent boiler is termed a close-coupled system, which has the potential for a higher efficiency than is achievable with direct combustion of most fuels such as biomass. High-moisture feedstocks have lower flame temperatures, which can result in particulate and tar emissions and lower boiler efficiencies.

Once gasified, however, the moisture is in the vapor state and improved combustion efficiencies can be achieved. Nevertheless, high-moisture-content fuel gases may have undesirable characteristics for existing equipment, so some degree of predrying may in any case be required.

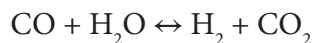
There is considerable interest in using catalysts to enhance the performance of both pyrolysis and gasification systems. As biomass contains low concentrations of sulfur and other catalyst poisons, the rapid deactivation of some catalysts that occurs with fossil fuels is not a problem. Alkali metal carbonates have been shown to increase the rate and extent of low temperature wood gasification. The use of these catalysts is discussed in Section 4.4 in connection with coal gasification. As mentioned, biomass materials have a high-volatile-matter content, and the small amount of char remaining on rapid pyrolysis is highly reactive relative to coal chars. The role of a catalyst would therefore seem to be more one of controlling gas phase reactions rather than promoting gas yields.

Gasification Chemistry

When fuel is fed to a gasifier, water and volatile matter are released fast and a char residue is left to react further. The char gasification is what mainly controls the conversion achieved in the process. From solid carbon, product gas is formed according to the following main reactions:



In addition to the reactions of solid carbon, the most important reaction is the water-gas shift reaction, which takes place in the gas phase:



The product gas generally contains large amounts of hydrogen and carbon monoxide and a small amount of methane, as well as carbon dioxide and steam, and in air gasification nitrogen. In addition, a significant amount of other organic components in the gas, known as tar, is formed.

See also: Gasification; Gasification (Volume 3: Coal).

Gasification of Biomass

Gasification of biomass is a process in which solid biomass fuels are broken down by the use of heat in an oxygen-starved environment, to produce a combustible gas. Biomass fuels that can be gasified include wood, charcoal, rice husks, coconut shells, and a variety of other dry biomass materials. A biomass gasification system consists primarily of a reactor into which fuel is fed along with a limited (less than stoichiometric or that required for complete combustion) supply of air. Heat for gasification is generated through partial combustion of the feed material. The resulting chemical breakdown of the fuel and internal reactions result in a combustible gas usually called producer gas.

The primary objective of biomass gasification is to convert as much of the feed material as possible to a gaseous product. A secondary objective might be to increase the H_2/CO ratio of the gas over that obtained in pyrolysis so as to facilitate downstream upgrading. This latter objective can be effectively achieved using a subsequent gas shift step. Apart from upgrading to synthetic natural gas, liquid products can be produced by the Fischer-Tropsch synthesis.

In the process, the feedstock (biomass which may also be co-gasified with solid waste) is transformed into gas, which can be burned directly as fuel or used as a raw material for synthesis gas or hydrogen production. Considerable environmental importance rests upon the development of highly efficient power cycles and on the production of liquid biofuels and hydrogen from these renewable energy sources. Even though gasification technologies have recently been successfully demonstrated, they continue to be expensive relative to energy production based on fossil fuels. Strong drivers to develop and commercialize biomass and waste gasification exist, however, in face of the urgent need to increase the rates of biomass use and waste recycling and to improve the efficiency of their use in electricity production.

The feedstock entering a gasifier is first dried by rising hot gases. Further heating results in devolatilization and pyrolysis reactions. In the next stage, temperatures are sufficiently high for the gasification reactions to proceed.

The raw gas produced on gasification of a carbonaceous feedstock has a low-to-medium calorific value, depending on whether air or oxygen is used as the oxidant in directly heated gasifiers. The product from indirectly heated gasifiers, in which an inert material is typically used to transfer the heat from an external source, is generally a medium-heat content gas. The energy in these gases could theoretically be utilized directly, for example by generation of

electricity, either by raising steam in a boiler or by combustion in a gas turbine. However, the gases produced on gasification do not satisfy the clean fuel criteria, and so further processing is necessary. Removal of pollutant gases such as ammonia and hydrogen sulfide, and inert gases such as carbon dioxide, is an obvious requirement. Gas purification processes do not involve reactions of the active gas components.

Gasification with air results in a low-heat content gas that can be used for combined cycle electricity generation. Increased efficiencies attained with combined cycle systems gasifying conventional fossil fuels arise in part from the more effective pollution control techniques that may be used. In the case of biomass, sulfur concentrations are low, so its direct combustion does not require an attendant energy-consuming flue gas desulfurization step. Other factors including nitrogen oxide emissions, the inherent greater efficiency of gas turbines, and the limited scale of operations, will determine whether or not combined cycle generation with biomass will be more viable than conventional steam-electric generation.

If heat or steam is the desired product, then again air gasification appears to offer little advantage over direct combustion as far as pollution control is concerned. It is possible that air gasification may prove useful as a means of providing a substitute fuel for existing gas-fired boilers.

A gasifier supplying fuel to an adjacent boiler is termed a *close-coupled system*, which has the potential for a higher efficiency than is achievable with direct combustion of most fuels such as biomass. High-moisture feedstocks have lower flame temperatures, which can result in particulate and tar emissions and lower boiler efficiencies. Once gasified, however, the moisture is in the vapor state and improved combustion efficiencies can be achieved. Nevertheless, high-moisture-content fuel gases may have undesirable characteristics for existing equipment, so some degree of pre-drying may in any case be required.

There is considerable interest in using catalysts to enhance the performance of both pyrolysis and gasification systems. As biomass contains low concentrations of sulfur and other catalyst poisons, the rapid deactivation of some catalysts that occurs with fossil fuels is not a problem. Alkali metal carbonates have been shown to increase the rate and extent of low-temperature wood gasification.

Biomass materials have a high-volatile-matter content, and the small amount of char remaining on rapid pyrolysis is highly reactive relative to coal chars. The role of a catalyst would therefore seem to be more one of controlling gas phase reactions rather than promoting gas yields.

A gasification system consists of four main stages which are (i) feeding, (ii) gasifier, (iii) gas cleaning, and (iv) utilization of combustible gas.

Feeding is important, and especially the feeding of pressurized systems is seen as problematic (such as mechanical issues and tight gas issues). Some genius level engineering solutions are required in this area. Low-pressure gasifiers can adopt a lot of the technology developed for combustion of biomass.

Biomass gasification systems offer several advantages over direct combustion systems. Gasification reduces corrosion compared to direct combustion because of the lower temperatures in the gases. Gasifiers can convert the energy content of a feedstock to hot combustible gases at 85% to 90% thermal efficiency. In addition, the fuel throughput per unit area is greater for gasification than combustion, which means that smaller gasification units can process the same amount of fuel as larger combustion units. In addition, approximately 80% of the usable energy is in the form of chemical energy in the gas. A final advantage is that, if desired, the materials that cause slagging can be removed at relatively high temperatures through a gas clean-up process. These last two statements imply that the gas can be cleaned up and used at higher temperatures without significant loss of sensible heat, although the costs to do so can be considerable.

Characterization of biomass for gasification and other thermochemical processes is often based solely on determination of the general fuel characteristics (e.g., proximate and ultimate analysis, heating values, ash fusion temperatures, etc.), the chemical composition and physical properties relevant for gasification. Also included are particle shape, particle size and size distribution, flow properties, and bulk density.

Waste-based fuels are characterized in the same way as the conventional fuels. Mixed paper waste is an attractive energy source since it is relatively homogeneous and mostly free of putrescible matter, metals, and other non-combustible constituents. Minimal processing is required to convert it to fuel for gasification, and, when processed into densified fuel, the heating value is close to that of wood.

Each type of biomass has its own specific properties which determine its performance as a fuel in gasification plants. The most important feedstock properties relating to gasification are (i) moisture content, (ii) mineral matter

content, (iii) elemental composition, (iv) bulk density and morphology, and (5) volatile matter content. For thermal conversion processes like gasification, preference is given to relative dry biomass feedstocks because a higher-quality gas is produced, i.e., higher heating value, higher efficiency, and lower tar levels.

The amount of ash produced by different type of feedstocks differs widely (0.1% for wood up to 15% w/w for some agricultural products) and influences the design of the reactor, particularly the ash removal system. The chemical composition of the ash is also important because it affects the melting behavior of the ash. Ash melting can cause slagging and channel formation in the reactor. Slag can ultimately block the entire reactor.

The elemental composition of the fuel is important with regard to the heating value of the gas and to the emission levels. The production of nitrogen and sulfur compounds is generally small in biomass gasification because of the low nitrogen and sulfur content in biomass.

Bulk density refers to the weight of material per unit of volume and differs widely between different types of biomass. Together with the heating value, the bulk density of the feedstock determines the energy density of the gasifier feedstock, i.e., the potential energy available per unit volume of the feedstock. Biomass of low bulk density is expensive to handle, transport, and store. Apart from handling and storing behavior, the bulk density is important for the performance of the biomass as a fuel inside the reactor: a high voidage tends to result in channeling, bridging, incomplete conversion, and a decrease in the capacity of the gasifier. The bulk density varies widely (100-1,000 kg/m³) between different biomass feedstocks, as a result of the manner in which the biomass becomes available (chips, loose, baled, etc.).

The amount of volatile products has a major impact on the tar production levels in gasifiers. Depending on the gasifier design, the volatiles leave the reactor at low temperatures (updraft gasifiers) or pass through a hot incandescent oxidation zone (downdraft gasifiers) where they are thermally cracked. For biomass materials, the volatile matter content varies between 50 and 80%.

See also: Biomass Gasification, Gas Cleaning, Gasification .

Gasification of Biomass – Feedstock Preparation

Different biomass characteristics results in the necessity to pretreat/process different types of biomass feedstocks when they are going to be used as a gasifier fuel. The need for a suitable feed preparation system is well known but unfortunately poorly understood.

Feedstock preparation is required for almost all types of biomass materials because of a large variety in physical, chemical, and morphological characteristics. The degree to which any specific pretreatment is desirable will depend on the details of the gasifier plant, such as capacity and type of reactor (downdraft gasifiers are more strict to uniform fuel specifications than updraft gasifiers) (Table G-6).

Any listed fuel characteristics can be influenced by pretreatment process – for example, mineral additives can influence the ash melting behavior. However, the most important pretreatment technologies are drying, sizing, and densification. Other pretreatment technologies like screening and sifting are only of importance to specific materials like heavy contaminated demolition materials such as sand, paper, plastic, non-ferrous metals, ferrous metals, and demolition wood.

Table G-6 General guidelines for fuel requirements for different gasifier types.

Gasifier type:	Downdraft	Updraft	Cross draft
Size, mm	20-100	5-100	40-80
Moisture, % w/w	<20	<50	<7
Bulk density	>500	>400	>400
Ash yield, % w/w	<5	<15	<6
Ash melting point °C	>1,250	>1,250	>1,250

Sizing of the feedstock may be necessary as different sizes are specified for different types of gasifiers. For small-scale fixed-bed gasifiers, cutting and/or sawing of wood blocks is the preferred form of fuel preparation. Chipped

wood is preferred for larger-scale applications. The size range of chips can be chosen by screening such that the fuel is acceptable for a specific gasifier type. For medium- and large-scale fixed-bed gasifiers, wood chips from forestry or wood processing industries are produced by crushers, hammermills, shredders, and/or mobile chippers (particularly for thinnings from landscape conservation activities). Most of these sizing apparatus are provided with a screen. Depending on the feedstock morphology and characteristics (hardness), the throughput or capacity of these techniques varies widely.

Drying of the fuel is advisable if fresh wet materials (moisture content 50-60% on wet basis) are to be gasified. As outlined previously under § 1.2.3, lowering the moisture content of the feedstock is associated with a better performance of the gasifier. Utilizing the exhaust gases from an internal combustion engine is a very efficient way to do so. The sensible heat in engine exhaust is sufficient to dry biomass from 70% down to 10%. Rotary kilns are the most applied dryers. The energy costs of drying are high, but these can be outweighed by the lower downstream gas cleaning requirements for dried feed.

Briquetting or pelletization is an important technique to densify biomass materials for increasing the particle size and bulk density. The reasons for densification are (i) the densified biomass is less expensive to transport, (ii) the densified products are easier to store and handle, and (iii) densification enables certain biomass feedstocks to be gasified in a specific gasifier.

The sequence of pretreatment technologies depends on the type and characteristics of the biomass material and the requirements of the gasifier fuel. The following aspects are important in the biomass pretreatment sequence which is (i) the larger materials such as window-frames need to be sized in two or more steps, (ii) the wet materials like waste from public gardens requires more drying energy compared to dry materials like demolition wood, (iii) artificial drying of larger materials requires more time compared to fine materials like sawdust, (iv) wet materials like thinnings, waste from public gardens, and green waste (vegetable, fruit, and garden) have a generally small particle size, (v) screening of wet materials is a less efficient process compared to screening of dry materials, and (vi) hammermills can only be applied for relatively dry materials; for sizing of wet materials, chippers provided with a knife must be applied.

See also: Biomass Gasification, Gasification.

Gasification Reactors

Three principal reactor types are employed in gasifier design: the moving packed bed, the fluidized bed, and the entrained flow reactor. A fourth type, the molten media reactor (or molten salt reactor), could be grouped together with the entrained flow reactor, but is sufficiently distinctive in its operation that it should be treated separately.

Fixed bed gasifiers are suitable for small-scale processes, i.e., less than 10 MW. Feedstock flows by gravity, while the gas flow can be either updraft or downdraft. Ideally, the feedstock should be piece-like and fairly homogeneous to flow smoothly in the reactor. In practice, however, it contains fines and fibrous material, which cause problems in the fuel flow leading to operational problems. The flow problems can be avoided by applying a new type of technology (novel fixed-bed gasifier), in which the flow is forced.

Fluidized bed reactors could solve the problems related to non-homogeneity of the feedstock, but they are too expensive in a small scale. In fluidized bed technology, the feedstock must be crushed to millimeter size before it is gasified in either bubbling or circulating mode. These gasifiers are suitable for scales up to hundreds of megawatts. Recently, fluidized bed technology was applied for wastes where the product gas is combusted in a pulverized coal-fired boiler. The same method has been used to recover aluminum from the reject produced in liquid packaging board (LPB) recycling. The circulating fluidized bed has been demonstrated to be particularly suited for fuels containing high contents of alkali metals, where ash sintering problems can be avoided by using limestone and special arrangements with the feeds.

In the third type of gasifier, the entrained flow gasifier, pulverized fuel is gasified at high temperature. This is regarded as one of the optional processes for liquid fuel manufacture from biomass and wastes. High pressure gasification based on the entrained flow process can be applied to improve the energy recovery from black liquor.

The reactor type strongly influences the temperature distribution, and in this way the gas and residue products. The reaction temperature varies from approximately 815 to 1,925°C (1,500 to 3,500°F), with each type of gasifier covering

a specific range. The exception to this is the molten media gasifier whose temperature and, to some extent, characteristics of operation are determined by the melt employed.

At high temperatures, a synthesis gas is produced and at low temperatures, methane formation is favored. As the overhead product is affected, so is the residue. Gasifiers in which the temperature is low enough that the ash does not melt are sometimes referred to as dry bottom gasifiers. High temperature gasifiers in which molten ash (slag) is formed are called slagging gasifiers. The slagging temperature is dependent on the ash composition, but for most coals lies roughly in the range 1,200 to 1,800°C (2,190 to 3,270°F).

In the terminology of gasifier technology, the term fixed bed gasifier refers to a gasifier in which a packed bed of fuel is supported by a grate or by other means and maintained at a constant depth above the support. The fuel moves downward under the action of gravity from the top of the gasifier, through the gasification and combustion zones, and the residue is discharged at the bottom. Within the reactor classes, this is a moving packed bed or a moving bed reactor.

Moving bed gasifiers operate with countercurrent flow, use either steam and oxygen or steam and air, and the residue may be slag or dry ash plus any unconverted carbon. Undried feedstock particles that range in size between 3 and 50 mm are fed into the top of the gasifier, with the size range dependent on the particular process. The particle sizes must be sufficiently large (>3 mm) in order that they not be carried out overhead by the exiting product gases. Smaller particles, termed fines, must be removed from the feedstock, not only because of the carry-over problem, but also because they tend to clog the bed and offer a high resistance to the upward flowing gases.

The feedstock passes downward through the upward flowing gases, first being heated, then devolatilized, and then still lower down gasified. The bottom of the coal bed is the combustion zone, with the residue of the combustion cooled by the steam/oxygen or steam/air mixture entering from the bottom before it is discharged. The downward movement of the bed is relatively slow, with average linear velocities on the order of 0.5 m/h in atmospheric steam/air gasifiers and 5 m/h in high pressure steam/oxygen gasifiers. Feedstock residence times are correspondingly shorter with the higher velocity beds, and are typically on the order of 0.5 to 1 hour for the high pressure steam/oxygen gasifiers and some ten times longer for atmospheric steam/air gasifiers.

Temperatures in the combustion zone are mainly a function of the relative level of the oxidant. In atmospheric steam/air gasifiers, temperatures do not exceed the ash melting point. Steam/oxygen gasifiers may, however, be either dry ash or slagging depending on the amount of steam blown into the gasifier in relation to the amount of oxygen.

In dry ash gasifiers, a large quantity of steam is blown in, which holds down the temperature by virtue of its high heat capacity, and because the steam-carbon gasification reaction is endothermic. The excess steam does not participate in the reaction and is recovered from the product gases as dirty water. The maintenance of lower combustion temperatures by excess steam addition is critical for gasifiers designed for dry ash operation, since if the ash melts, it then cannot be handled on a supporting grate.

The excess steam requirement can be overcome by operating at high temperatures in a slagging mode. By deliberately operating at high temperatures, excess steam is no longer required to hold down the temperature. A second, but important, effect is that the rate of the carbon-steam reaction is enhanced at elevated temperature resulting in improved steam utilization and little undecomposed steam in the product gases. The absence of undecomposed steam coupled with lower carbon dioxide contents, because of the higher combustion temperatures, minimizes the amount of diluent gases that pass through the gasifier. The result is a higher product gas output, all else being equal. The penalty for this mode of operation is that handling of molten slag is required. The Lurgi gasifier, which was first run commercially in 1936, has been developed to operate in both the dry ash and slagging modes.

Combustion temperatures are also dependent on the reactivity of the feedstock. Less reactive feedstocks attain higher maximum combustion temperatures and require a higher steam/oxygen ratio to hold the temperature below a given ash melting point.

An advantage of the moving bed gasifier is that the countercurrent direct contact heat exchange that takes place within the gasifier results in relatively high overall conversion efficiency with a minimum of heat loss.

Entrained flow gasifiers all use feedstock pulverized to a size on the order of 75 μ m. Oxygen or air together with steam generally is used to entrain the feedstock, which is injected through nozzles into the gasifier burner. Hot product gas, or in the case of hydrogasification hot hydrogen, may also be used to entrain the feedstock and at the same time gasify it. In the Texaco gasifier, the solids are carried in a water slurry. However, in a preheater, the water is turned into steam, and it is the steam plus feedstock that is blown into the reactor.

Entrained flow reactors have the advantage of having high throughput rates, especially with higher pressure operation. But because they are co-current flow systems, they are not the most efficient thermally. Moreover, the high off gas temperature, that is the temperature of the gas coming off the top of a gasifier, introduces additional losses through the requirement for irreversible quenching. The high temperature environment also imposes severe operating conditions, including the problem of mineral slag handling and removal.

Fluidized bed gasifiers are fed with pulverized or crushed feedstock that is lifted in the gasifier by feed and product gases. In single stage, directly heated gasifiers, a steamy oxygen or steam/air mixture is injected near the bottom of the reactor, either co-current or countercurrently to the flow of the feedstock. The rising gases react with the feedstock and at the same time maintain it in a fluidized state. As feedstock gasification occurs, the larger size mineral particles, which are approximately twice as dense as the carbonaceous material, fall down through the fluidized bed together with larger char particles. The smaller and low-density particles of unconverted carbon, char, and ash are carried upward with the product gases.

Advantages of fluidized beds include good mixing of the solids and a uniform temperature bed, with rapid temperature equilibration between the solids and gases. As a consequence, fluidized bed gasifiers have the advantage that there is efficient heat transfer from the exothermic to the endothermic regions, and therefore, the gasification reactions reach equilibrium quickly, resulting in relatively high throughputs. A disadvantage of most fluidized bed gasifiers is the potential for carry-over of solids in the product gas, and a means of removing this carry-over has to be incorporated.

In molten media gasifiers, the feedstock is dispersed into a molten carrier, which generally takes part in the gasification and acts as a heat source. The feedstock particles are, for the most part, entrained in the slag, which promotes the gasification reactions and certain constituents, such as iron oxide, act as oxygen-transfer agents through oxidation and reduction reactions.

The temperature in molten media gasifiers depends upon the melt, but as a group, they have the advantage that they can accept all types of feedstocks and provide an efficient heat sink for the promotion of gasification reactions. However, a limitation is that the processes must handle the molten media and, for example, in the case of molten salt, regenerate and recycle an extremely corrosive material.

See also: Biomass Gasification, Gasification, Gasification (Volume 3: Coal).

Gasifiers

A gasifier is a device for converting solid fuel into gaseous fuel; in biomass systems, the process is referred to as pyrolytic distillation. Some few gasifiers have already been in operation for several decades, and a number of gasification processes are under industrial development at pilot and demonstration scale.

A range of feedstock is available for gasification and varies from clean biomass to waste fuels containing different amounts of ash, alkaline, and emission precursors like nitrogen chlorine, and sulfur. A wide range of applications has been developed and demonstrated for (co)-firing in boilers/furnaces, gas engines, and combined cycles. For some applications, it is important to increase gas-heating value. Low heating value gas has some impact on power generation, which has to be considered such as power de-rating and flame stability.

See also: Gasification – Reactors

Gasifiers – Bubbling Fluidized Bed Gasifier

The bubbling fluidized bed gasifier is one of the most popular designs for biomass gasification. The gasifier consists of a vessel in which the gasifying agent is introduced upward at a velocity fast enough to agitate the bed material which sits at the bottom part of the gasifier and to maintain the required temperature. Biomass is fed from the side into the hot bed, where devolatilization occurs. Char particles and volatiles (tar precursors) are gasified and cracked by contact with the hot fluidized bed. Additional gasifying agent can be supplied in a second zone located above the bed with the aim of converting entrained unconverted volatiles and char particles into fuel gas. A final flue gas

with low to medium tar content is produced. Ash is separated from the synthesis gas in gas-solid separation units downstream.

The gasifying agent can be supplied in two different zones. The first zone is within the fluidized bed in order to maintain the required temperature. The second zone is located above the bed, and it aims to convert entrained unconverted volatiles and char particles into fuel gas.

See also: Gasification.

Gasifiers – Circulating Fluidized Bed Gasifier

The circulating fluidized bed (CFB) gasifier is a type of fluidized bed gasifier that utilizes a recirculating loop for even greater efficiency of gasification while achieving lower production (and emission) of pollutants. The gasifier is a natural extension of the bubbling fluidized bed gasifier, with cyclones or other separators employed to capture and recycle solids in order to extend the solids' residence time. The riser of a circulating fluidized bed gasifier operates in either the turbulent or fast fluidization flow regime.

Circulating fluidized beds operate in the regime of fast fluidization, while the bubbling fluidized beds operate in the regime of bubbling fluidization. This difference has a number of consequences for the gasification process, depending on which type of the fluidized bed reactor. In a circulating fluidized bed operating in the fast fluidization flow regime, particles tend to migrate outwards toward the wall, driven by fluid-particle interactions and boundary effects, and descend along the wall, while dilute upon is maintained in the inner core. As a result of the higher concentration of particles in the wall region, there is a reducing region there, with augmented methane, hydrogen, and carbon monoxide concentrations

See also: Gasification.

Gasifiers – Cross Draft Gasifier

The cross draft gasifier is one of the simplest types of gasifier. The reactor for this gasification is much like the updraft gasifier in that the fuel will enter from the top and the thermochemical reaction will occur progressively as this fuel descends into the reactor. The crucial difference is that the air will be entering the gasifier from the side of the reactor, rather than from the top or the bottom. The start-up time for this reactor is relatively short, and high temperatures can be attained using this type of gasification. Cross draft gasification isn't seen very often in commercial processes mainly because other gasification methods offer more flexibility with respect to fuel types; this type of gasification doesn't handle fuel that has a high tar content, and bridging can be a consequence of the particle size of the fuel.

Although cross draft gasifiers have certain advantages over updraft and downdraft gasifiers, they are not ideal. The disadvantages such as high exit gas temperature, poor CO₂ reduction, and high gas velocity are the consequences of the design. Unlike downdraft and updraft gasifiers, the ash bin, fire, and reduction zones in cross draft gasifiers are separate. These design characteristics limit what kind of fuel can be used, restricting it to only low ash fuels such as wood, charcoal, and coke. The load following ability of cross draft gasifier is quite good due to concentrated zones which operate at temperatures up to 1,200°C. Startup time (5-10 minutes) is much faster than that of downdraft and updraft units. The relatively higher temperature in cross draft gas producer has an obvious effect on exit gas composition such as high carbon monoxide and low hydrogen and methane content when dry fuel such as charcoal is used. Cross draft gasifier operates well on dry air blast and dry fuel.

See also: Gasification.

Gasifiers – Downdraft Gasifier

In an updraft gasifier (also referred to as the co-current gasifier), there is a problem of tar entrainment in the product gas leaving stream. A solution is to have primary gasification air introduced at or above the oxidation zone in the gasifier. The produced gas is taken out from the bottom; hence, fuel and gas move in the same direction. On the way down, the acid

and tarry distillation products from the fuel must pass through a glowing bed of charcoal and therefore are converted into permanent gases hydrogen, carbon dioxide, carbon monoxide, and methane. Depending on the temperature of the hot zone and the residence time of the tarry vapors, more or less a complete breakdown of the tars is achieved.

The main advantage of downdraft gasifier lies in the possibility of producing tar-free gas for engine operation. However, in practice, very rarely tar-free gas is produced but the percentage of tar leaving in product stream is considerably lower than leaving through the updraft gasifier.

The main disadvantage is that downdraft gasifier cannot be operated with a range of different feedstocks. Low density feedstock gives rise to flow problems and excessive pressure drop. High ash content coal also gives more problem with this kind of gasifier than updraft gasifier. Another disadvantage is the lower efficiency, since there is no provision internal exchange compare to updraft gasifier. The product stream also has low calorific value.

See also: Gasification.

Gasifiers – Entrained Bed Gasifier

In an entrained bed gasifier, the feedstock and oxygen enter in co-current flow. The feedstock is grounded to a size of 100 μm or less to promote mass transfer and allow transport of solids using gas flow. The key characteristics of entrained flow gasification are high and uniform temperatures (usually more than 1,000°C, >1,830°F) and the short residence time of the fuel within the gasifier. Because of the high temperatures, high conversion is possible. The high temperature operation requires high oxygen demand for these types of processes.

In the process, ash is withdrawn in the molten form. Solids fed into the gasifier must be very finely ground and homogeneous, which in turn means that entrained flow gasifiers are not suitable for feedstocks such as biomass or wastes, which cannot be readily pulverized.

See also: Gasification.

Gasifiers – Fluidized Bed Gasifier

The operation of both updraft and downward draft gasifiers is influenced by the morphological, physical, and chemical properties of the fuel. Problems commonly encountered are (i) lack of bunker flow, (ii) slagging, and (iii) extreme pressure drop over the gasifier.

In the fluidized bed gasifier, air is blown through a bed of solid particles at a sufficient velocity to keep these in a state of suspension. The bed is originally externally heated, and the feedstock is introduced as soon as a sufficiently high temperature is reached. The fuel particles are introduced at the bottom of the reactor, very quickly mixed with the bed material and almost instantaneously heated up to the bed temperature. As a result of this treatment, the fuel is pyrolyzed rapidly which results in a component mix with a relatively large amount of gaseous materials. Further gasification and tar-conversion reactions occur in the gas phase. Ash particles are also carried over the top of the reactor and have to be removed from the gas stream if the gas is used in engine applications. To remove ash particles, cyclone and candle filter are used.

The major advantage of fluidized bed is processing of feedstock. This type of gasifier are mostly used for high ash coal and biomass. Since the temperature is below the ash softening temperature, handling of ash is relatively simple. A drawback of the fluidized bed gasifiers is the high tar content in the produced synthesis gas and incomplete carbon conversion.

See also: Gasification.

Gasifiers – Moving Bed Gasifier

In the moving bed gasifier, the feedstock enters at top and moves downward through gravity and is gasified by the upcoming countercurrent air/oxygen and steam mixture. The hot synthesis gas from gasification zone is used to pre-heat and pyrolyze the downward flowing feedstock. With this process, the oxygen consumption is low, but pyrolysis

products are present in the product synthesis gas. This gasifier can operate on coarse (lump) feedstock, and the outlet temperature of syn gas is generally low.

See also: Gasification.

Gasifiers – Updraft Gasifier

The updraft gasifier (also referred to as the co-current gasifier) is the oldest and simplest of all gasifier types. The air comes in at the bottom and produced syn gas leaves from the top of the gasifier. Near the grate at the bottom, combustion reaction occurs; above that, reduction reaction occurs. In the upper part of the gasifier, heating and pyrolysis of the feedstock occur as a result of heat transfer by forced convection and radiation from the lower zones. Tars and volatile produced during the reaction will leave along with the syn gas at the top of the gasifier, which will be later separated by use of cyclone and candle filter.

The major advantages of this type of gasifier are (i) simplicity, (ii) high charcoal burn out, and (iii) internal heat exchange leading to low temperature of exit gas and high equipment efficiency. This gasifier can work with several kinds of feedstock ranging from coal to biomass.

The major drawbacks of the gasifier result from the possibility of channeling in the equipment, which can lead to oxygen break-through and dangerous, explosive situations and the necessity to install an automatic moving grate.

See also: Gasification.

Gas Laws

Many gas streams produced as alternative fuels are natural gas, and the petroleum-derived gases before separation, are typically a non-ideal gas and follow the gas law:

$$PV = nZRT$$

P is the pressure, V is the volume, T is the absolute temperature (degree Kelvin), Z is the compressibility factor, n is the number of kilo-moles of the gas, and R is the gas constant. For example, if all other factors remained constant, when the volume of a certain mass of gas is reduced by 50%, the pressure would double and so on. As a gas, it would expand to fill any volume it is in. However, the compressibility, Z, is the factor that differentiates natural gas from an ideal gas. For methane, Z is 1 at 1 bar but decreases to 0.85 at 100 bar, both at 25°C, that is, it compresses to a smaller volume than the proportional relationship.

Boyle's Law: The Pressure-Volume Law

Boyle's law or the *pressure-volume law* states that the volume of a given amount of gas held at constant temperature varies inversely with the applied pressure when the temperature and mass are constant.

$$V \propto \frac{1}{P}$$

Another way to describe it is saying that their products are constant.

$$PV = C$$

When pressure increases, the volume decreases. When volume increases, the pressure decreases. From the equation above, this can be derived:

$$P_1 V_1 = P_2 V_2 = P_3 V_3 \text{ etc.}$$

This equation states that the product of the initial volume and pressure are equal to the product of the volume and pressure after a change in one of them under constant temperature.

Charles' Law: The Temperature-Volume Law

This law states that the volume of a given amount of gas held at constant pressure is directly proportional to the Kelvin temperature.

$$V \propto T$$

A constant can be inserted:

$$V/T = C$$

As the volume increases, the temperature also increases, and vice-versa. Also same as before, initial and final volumes and temperatures under constant pressure can be calculated.

$$V_1/T_1 = V_2/T_2 = V_3/T_3 \text{ etc.}$$

Gay-Lussac's Law: The Pressure Temperature Law

This law states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature.

$$P \propto T$$

A constant can be inserted:

$$P/T = C$$

As the pressure increases, the temperature also increases, and vice-versa. Also, initial and final volumes and temperatures under constant pressure can be calculated:

$$P_1/T_1 = P_2/T_2 = P_3/T_3 \text{ etc.}$$

Avogadro's Law: The Volume Amount Law

This law gives the relationship between volume and amount when pressure and temperature are held constant. Remember amount is measured in moles. Also, since volume is one of the variables, that means the container holding the gas is flexible in some way and can expand or contract. If the amount of gas in a container is increased, the volume increases. If the amount of gas in a container is decreased, the volume decreases:

$$V \propto n$$

A constant can be inserted:

$$V/n = C$$

This means that the volume-amount fraction will always be the same value if the pressure and temperature remain constant.

$$V_1/n_1 = V_2/n_2 = V_3/n_3 \text{ etc.}$$

The Combined Gas Law

In the Combined Gas Law, the relevant data from above can be combined into one proportion:

$$V \propto \frac{T}{P}$$

The volume of a given amount of gas is proportional to the ratio of its Kelvin temperature and its pressure. A constant can be inserted:

$$PV/T = C$$

As the pressure increases, the temperature also increases, and vice-versa. Also same as before, initial and final volumes and temperatures under constant pressure can be calculated:

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 = P_3 V_3 / T_3 \text{ etc.}$$

Ideal Gas Law

The previous laws all assume that the gas being measured is an *ideal gas*, a gas that obeys them all exactly. But, over a wide range of temperature, pressure, and volume, real gases deviate slightly from ideal. Since, according to Avogadro, the same volumes of gas contain the same number of moles, chemists could now determine the formulas of gaseous elements and their formula masses. The ideal gas law is:

$$PV = nRT$$

where n is the number of moles and R is the *universal gas constant* and is equal to approximately 0.0821 L-atm/mole-K.

Other Forms of the Gas Law

If the definition of the mole is included in the equation, the result is:

$$PV = gRT/FW$$

or

$$FW = gRT/PV$$

This equation provides a convenient way of determining the formula weight of a gas if the mass, temperature, volume, and pressure of the gas are known (or can be determined).

Dalton's Law of Partial Pressures

Dalton's Law of Partial Pressures states that the total pressure of a mixture of non-reacting gases is the sum of their individual partial pressures.

$$P_{\text{total}} = P_a + P_b + P_c + \dots$$

or

$$P_{\text{total}} = n_a RT/V + n_b RT/V + n_c RT/V + \dots$$

or

$$P_{\text{total}} = (n_a + n_b + n_c + \dots)RT/V$$

The pressure in a flask containing a mixture of 1 mole of 0.20 mole O₂ and 0.80 mole N₂ would be the same as the same flask holding 1 mole of O₂.

Partial pressures are useful when gases are collected by bubbling through water (displacement). The gas collected is saturated in water vapor which contributes to the total number of moles of gas in the container.

Non-Ideal Gases

The ideal gas equation ($PV=nRT$) provides a valuable model of the relations between volume, pressure, temperature, and number of particles in a gas. As an ideal model, it serves as a reference for the behavior of real gases. The ideal gas equation makes some simplifying assumptions which are obviously not quite true. Real molecules do have volume and do attract each other. All gases depart from ideal behavior under conditions of low temperature (when liquefaction begins) and high pressure (molecules are more crowded so the volume of the molecule becomes important). Refinements to the ideal gas equation can be made to correct for these deviations. The van der Waals equation for n moles of gas is:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

See Table G-7

Table G-7 Empirically determined values for the constants a and b .

Molecule	a (liters ² -atm/mole ²)	b (liters/mole)
H ₂	0.2444	0.02661
O ₂	1.360	0.03183
N ₂	1.390	0.03913
CO ₂	3.592	0.04267
Cl ₂	6.493	0.05622
Ar	1.345	0.03219
Ne	0.2107	0.01709
He	0.03412	0.02370

Finally, a *real gas*, as opposed to an *ideal gas*, refers to an assumption base where the following are taken into account: (i) compressibility effects, (ii) variable heat capacity, (iii) van der Waals forces, (iv) non-equilibrium thermodynamic effects, and (v) effects from molecular dissociation and elementary reactions with variable composition. For most applications, such a detailed analysis is unnecessary and the ideal gas approximation is used. Real-gas models have to be used (i) near the condensation point of gases, (ii) near the critical point, and (iii) at high pressure.

The units of pressure that are used are pascal (Pa), standard atmosphere (atm), and torr. 1 atm is the average pressure at sea level, which is normally used as a standard unit of pressure. The SI unit is the pascal, and 101,325 pascals equals 1 atmosphere (14.7 psi). A torr is the same unit as the mm Hg (millimeter of mercury; thus, 760 torr equals 1 atmosphere.

See also: Ideal Gas, Ideal Gas Law.

Gas Liquids

Gas liquids (in the case of natural gas, referred to as natural gas liquids, NGLs) are the hydrocarbon liquids that condense during the processing of hydrocarbon gases that are produced from (in the case of alternate energy sources) a thermal process. These are ethane (C_2H_6), propane (C_3H_8), normal butane ($n-C_4H_{10}$), isobutane ($i-C_4H_{10}$), pentanes (C_5H_{12}), and even higher molecular weight hydrocarbons. When processed and purified into finished by-products, all of these are collectively referred to as gas liquids (GLs).

The recovery of the gas liquids (GLs) is typically accomplished by a cryogenic low temperature distillation process involving expansion of the gas through a turbo-expander followed by distillation in a demethanizing fractionating column. Some gas processing plants use lean oil absorption process rather than the cryogenic turbo-expander process. The residue gas from the gas liquids recovery section is the final, purified sales gas which is pipelined to the end-user markets.

The recovered stream of gas liquids is processed through a fractionation train consisting of three distillation towers in series: a de-ethanizer, a depropanizer, and a debutanizer. The overhead product from the de-ethanizer is ethane, and the bottoms are fed to the depropanizer. The overhead product from the depropanizer is propane, and the bottoms are fed to the debutanizer. The overhead product from the debutanizer is a mixture of normal and iso-butane, and the bottoms product is a C_5+ mixture. The recovered streams of propane, butanes, and C_5+ are each "sweetened" in a Merox process unit to convert undesirable mercaptans (RSH) into disulfides (RSSR) and, along with the recovered ethane, are the final gas liquids by-products from the gas processing plant.

See also: Gas Cleaning, Gas Liquids – Fractionation, Gas Processing.

Gas Liquids – Fractionation

The bottom liquid from the gas liquids recovery plant may be sold as a mixed product. This is common for small, isolated plants where there is insufficient local demand. The mixed product is transported by truck, rail, barge, or pipeline to a central location for further processing. Often, it is more economical to fractionate the liquid into its various components, which have a market value as purity products.

At the fractionation plant, liquids will be separated into commercial quality products and then delivered to the market by tankers (exports) and tank trucks (domestic consumption). The gas liquids are fractionated by heating mixed gas liquid streams and passing them through a series of distillation towers. Fractionation takes advantage of the differing boiling points of the various products. As the temperature of the gas liquids stream is increased, the lightest (lowest boiling point) product boils off the top of the tower as a gas where it is then condensed into a purity liquid that is routed to storage. The heavier liquid mixture at the bottom of the first tower is routed to the second tower where the process is repeated, and a different product is separated and stored. This process is repeated until the gas liquids stream has been separated into their components.

Fractionators are usually named for the overhead or top product. Therefore, a de-ethanizer implies that the top product is ethane; a depropanizer indicates that the top product is propane. Gas liquids are normally fractionated by boiling the lighter products from the heavier products, and the process can be adapted for application to gas liquids from alternate energy sources (such as biomass).

The first step in the fractionating sequence is to separate the ethane and propane (in the de-ethanizer), with the ethane going overhead and the propane and heavier components passing from the bottom of the fractionator.

The next step in the processing sequence is to separate the propane and the isobutene (in the depropanizer), with the propane going overhead and the isobutane and heavier components passing from the bottom of the depropanizer. The next fractionating step uses a debutanizer in which the separation of the butanes from the pentanes plus C_5+ stream is achieved. The butanes (both iso-butane and n-butane) pass overhead and the pentanes plus from the bottom of the fractionator. When it is desirable to do so, the butanes which pass overhead from the debutanizer may be separated into iso-butane and n-butane in a butane splitter or de-isobutanizer. The iso-butane passes overhead, and the n-butane is drawn from the bottom of the tower.

Depending on the market situation of each product, the number of fractionating columns may be varied. For example, when a market for liquefied petroleum gas (LPG) only exists during a portion of the year, an LPG mixture

could be produced overhead with natural gasoline produced as bottoms in the second tower, and the third tower would be shut down and not operated.

Fractionation of the gas liquids to produce purity products such as petrochemical- grade ethane feedstock or fuel grade propane may take place in a gas processing facility but more commonly occurs at another location, usually a regional market center.

See also: Gas Cleaning, Gas Liquids, Gas Processing

Gasohol

Gasohol is a mixture of 10% v/v anhydrous ethanol and 90% gasoline by volume; 7.5% anhydrous ethanol and 92.5% gasoline by volume; or 5.5% anhydrous ethanol and 94.5 percent gasoline by volume.

Ethanol (ethyl alcohol) and methanol (methyl alcohol) are two types of alcohol fuels. The use of pure alcohols in internal combustion engines is only possible if the engine is designed or modified for that purpose. However, in their anhydrous or pure forms, they can be mixed with gasoline in various ratios for use in unmodified automobile engines. Typically, only ethanol is used widely in this manner, particularly since methanol is toxic.

E10, sometimes called gasohol, is a fuel mixture of 10% ethanol and 90% gasoline that can be used in the internal combustion engines of most modern automobiles. E10 blends are typically rated as 2 to 3 octane higher than regular gasoline and are approved for use in all new US automobiles, and are mandated in some areas for emissions and other reasons. E10 and other blends of ethanol are considered to be useful in decreasing US dependence on foreign oil, and can reduce carbon monoxide (CO) emissions by 20 to 30% under the right conditions. Although E10 does decrease emissions of CO and greenhouse gases such as carbon dioxide by an estimated 2% over regular gasoline, it can cause increases in evaporative emissions and some pollutants depending on factors like the age of the vehicle and weather conditions.

Similar blends include E5 and E7. These concentrations are generally safe for recent engines that run on pure gasoline. Some regions and municipalities mandate that the locally-sold fuels contain limited amounts of ethanol. One way to measure alternative fuels in the United States is the gasoline-equivalent gallons (GEG).

E15 contains 15% ethanol and 85% gasoline. This is generally the greatest ratio of ethanol to gas that is recommended by auto manufacturers that sell vehicles in the United States, though it is possible that many vehicles can handle higher mixtures without trouble. Flexible-fuel vehicles (FFV) are designed to take higher concentrations, up to 96% v/v ethanol (and no gasoline).

E85 is a mixture of 85% ethanol and 15% gasoline, and is generally the highest ethanol fuel mixture found in the United States. This mixture has an octane rating of approximately 105. This is down significantly from pure ethanol but still much higher than normal gasoline 87 octane. The addition of a small amount of gasoline helps a conventional engine start when using this fuel under cold conditions. E85 does not always contain exactly 85% ethanol. In winter, especially in colder climates, additional gasoline is added (to facilitate cold start).

E95 designates a blend of 95% ethanol and 5% ignition improver and is used in some diesel engines where high compression is used to ignite the fuel, as opposed to the operation of gasoline engines where spark plugs are used. Because of the high ignition temperatures of pure ethanol, the addition of ignition improver is necessary for successful diesel engine operation.

E100 is ethanol with up to 4% water. Operation in ambient temperatures below 15°C (59°F) causes problems with pure ethanol for starting engines. The most common cold weather solution is to add an additional small gasoline reservoir to increase the gasoline content momentarily to permit starting the engine. Once started, the engine is then switched back to pure ethanol.

See also: Ethanol, Gasoline, Methanol.

Gas Oil

Gas oil is a liquid crude oil distillate with a viscosity and boiling range between kerosene and lubricating oil (230 to 260°C, 450 to 500°F). Gas oil boils between the kerosene and lubricating oil fractions and is used to produce diesel fuel and heating oil.

Distillation (fractionation) separates shale oil into groups only by their boiling-point ranges; impurities may remain. These include organic compounds containing sulfur, nitrogen, and oxygen, inorganic salts, and dissolved metals that were present in the crude feedstock.

The gas streams may contain constituents that might be otherwise fractionated into middle distillates (fuel oils) and lubricating oil. Vacuum distillation will also produce low-boiling vacuum gas oil and high-boiling vacuum gas oil as well as vacuum residuum. Generally, the vacuum gas oil streams are sent to the catalytic cracker to produce more gasoline streams.

Analogous to crude oil, shale oil can be distilled as a single (unblended) feedstock or as a blend with crude oil.

The feedstock is heated in a heat exchanger and furnace to approximately 750°F and fed to a vertical, distillation column at atmospheric pressure where most of the feed is vaporized and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lower-boiling (lower-boiling) fractions condense and are collected toward the top of the column, whereas higher-boiling (heavier) fractions, which may not vaporize in the column, are further separated later by vacuum distillation.

The distillation section comprising the atmospheric unit and the vacuum unit is required to have the greatest flexibility in terms of variable quality of feedstock and range of product yields. The atmospheric distillation unit is, in fact, a collection of distillation units that enable a fairly efficient degree of fractionation to be achieved. In contrast to the early units, which consisted of separate stills, a tower is used in the modern-day refinery.

Vacuum distillation evolved because of the need to separate the less volatile products, such as lubricating oils, from the crude oil without subjecting these high boiling products to cracking conditions. The boiling range of the highest boiling fraction obtainable at atmospheric pressure is limited by the temperature (approximately 350°C; ca. 660°F) at which the residue starts to decompose or crack, unless cracking distillation is preferred. When the feedstock is required for the manufacture of lubricating oils, further fractionation without cracking is desirable and this can be achieved by distillation under vacuum (reduced pressure) conditions.

See also: Refining.

Gasoline

Gasoline, also called gas (United States and Canada), or petrol (Great Britain) or benzine (Europe) is mixture of volatile, flammable liquid hydrocarbons derived from crude oil and used as fuel for internal-combustion engines. It is also used as a solvent for oils and fats. Originally a by-product of the crude oil industry (kerosene being the principal product), gasoline became the preferred automobile fuel because of its high energy of combustion and capacity to mix readily with air in a carburetor. Small quantities of various additives are common, for purposes such as tuning engine performance or reducing harmful exhaust emissions. Some mixtures also contain ethanol as a partial alternative fuel. In aviation, mogas, short for motor gasoline, is used to distinguish automobile fuel from aviation gasoline, or avgas.

Gasoline is a mixture of hydrocarbons that usually boil below 180°C (355°F) or, at most, below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have four to twelve carbon atoms in their molecular structure and fall into three general types: paraffins (including the cycloparaffins and branched materials), olefins, and aromatics. Gasoline is produced in a refinery as a blend of several streams. Initially, the fraction that is separated from crude oil by distillation (straight-run gasoline or straight-run naphtha) does not meet the required specifications for modern engines (in particular octane rating), but will form part of the blend. The various refinery streams blended together to make gasoline all have different characteristics. Some of the streams which contribute to the final gasoline product are:

1. Straight-run naphtha (referred to as virgin naphtha), which is produced directly from crude oil by distillation but has a low octane rating, low aromatics (depending on the crude oil), some naphthene derivatives (cycloalkane derivatives) and no olefin derivatives (alkene derivatives).

2. Gasoline from a catalytic cracking unit (FCC gasoline, cat gasoline) or cat cracked naphtha (FCC naphtha, cat naphtha), which is produced in a catalytic cracker, with a moderate octane rating, high olefin (alkene) content, and moderate aromatics level.
3. Hydrocrackate (high-, mid-, and low-boiling), which is produced in a hydrocracker, with medium-to-low octane rating and moderate-to-low levels of aromatics.
4. Reformate, produced in a catalytic reformer, with a high octane rating and high aromatic content, and low olefin (alkene) content.
5. Alkylate, produced in an alkylation unit, with a high octane rating and which is a pure paraffin (alkane) mix with branched chains.
6. Isomerase, which is obtained by isomerizing the pentane and hexane in low-boiling straight-run naphtha to yield their higher octane isomers.
7. Polymerase, which is obtained by the conversion of gaseous olefins, such as ethylene, propylene, and butylene into larger molecules in the gasoline range.

A typical gasoline is predominantly a mixture of paraffin derivative, naphthene derivatives (cycloalkane derivatives), and olefin derivatives (alkene derivatives). The exact ratios can depend on (i) the refinery where the gasoline is produced – not all refineries have the same suite of processing units, (ii) the feedstock used by the refinery, and (iii) the grade of gasoline, in particular the octane rating. Many countries set limits on the amount of aromatics in gasoline, benzene in particular, and olefin (alkene) content. This is increasing the demand for high octane pure paraffin (alkane) components, such as alkylate, and is forcing refineries to add processing units to reduce the benzene content.

Gasoline is highly volatile as measured by the Reid vapor pressure (RVP). The desired volatility depends on the ambient temperature: in hotter climates, gasoline components of higher molecular weight (lower volatility) are used. In hot climates, excessive volatility results in vapor lock where combustion fails to occur, because the liquid fuel has changed to a gaseous fuel in the fuel lines, rendering the fuel pump ineffective and starving the engine of fuel. This effect mainly applies to engine-mounted fuel pumps; a fuel pump located in the fuel tank, as in most modern automobiles, is much more resistant to vapor lock.

In cold climates, too little volatility results in cars failing to start; consequently, butane is often added to gasoline scheduled for use in coal climates.

An important characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to the abnormal combustion phenomenon known as pre-detonation (also known as knocking, pinging, spark knock, and other names). Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane and n-heptane. There are a number of different conventions for expressing the octane rating; therefore, the same fuel may be labeled with a different number, depending upon the system used.

Gas Processing

Gas cleaning (gas processing, gas refining) typically involves several processes to remove (i) oil; (ii) water; (iii) elements such as sulfur, helium, and carbon dioxide; and (iv) gas liquids. In addition, it is often necessary to install scrubbers and heaters at or near the wellhead that serve primarily to remove sand and other large-particle impurities. The heaters ensure that the temperature of the gas stream does not drop too low and form a hydrate with the water vapor content of the gas stream.

Many chemical processes are available for gas cleaning. However, there are many variables in the choice of process or the choice of reining sequence that dictate the choice of process or processes to be employed. In this choice, several factors must be considered such as (i) the types and concentrations of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide and carbon dioxide, gas may contain other contaminants, such as mercaptans (also called thiols, R-SH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes are also capable of removing the acid gas impurities to low levels when the acid gases are there in low-to-medium concentrations in the gas.

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

See also: Gas Cleaning.

Gas Processing – Chemical Activators

A series of chemical activators used with methyl diethanolamine offers the most cost-effective answer to complete or controlled acid gas removal from sour to very sour gas streams. However, there are limitations of even the most advanced activated methyl diethanolamine only-based gas treatment technologies in handling very highly acid gas loaded natural or associated oil field gases, especially for bulk acid gas removal when the acid gases are destined for cycling and/or disposal by re-injection.

See also: Gas Cleaning, Gas Purification.

Gas Processing – Process Selection

Natural gas found at the wellhead, although still composed primarily of methane, is by no means as pure and must go through a series of processing or refining operations. Major transportation pipelines usually impose restrictions on the make-up of the gas that is allowed into the pipeline. That means that before the gas can be transported, it must be purified, while the ethane, propane, butane, and pentane derivatives must be removed from the gas stream.

Gas cleaning consists of separating all of the various hydrocarbon derivatives, non-hydrocarbon derivatives, and fluids from the gas stream. Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users. The natural gas used by consumers is composed almost entirely of methane.

Raw natural gas comes from three types of wells: oil wells, gas wells, and condensate wells. Natural gas that comes from oil wells is typically termed associated gas. This gas can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). Natural gas from gas and condensate wells, in which there is little or no crude oil, is termed non-associated gas. Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate. Whatever the source of the natural gas, once separated from crude oil (if present), it commonly exists in mixtures with other hydrocarbon derivatives, principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds. In fact, associated hydrocarbon derivatives, known as natural gas liquids (NGLs), can be valuable by-products of natural gas processing. Natural gas liquids include ethane, propane, butane, iso-butane, and natural gasoline that are sold separately and have a variety of different uses, including enhancing oil recovery in oil wells, providing raw materials for oil refineries or petrochemical plants, and as sources of energy.

High partial pressures (50 psia) of acid gases enhance the probability of using a physical solvent. The presence of significant quantities of high-boiling hydrocarbon derivatives in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating.

Process selection is not easy, and a number of variables must be weighed prior to making a process selection. After preliminary assessment, it usually requires a study of relevant alternatives.

In general, the batch and amine processes are used for over 90% of all onshore wellhead applications. Amine processes are preferred when the lower operating cost, the chemical cost for this process, is prohibitive, and justifies the higher equipment cost. The key is the sulfur content of the feed gas where below 20-pound sulfur per day, batch processes are more economical, and over 100-pound sulfur per day amine solutions are preferred.

Gas Purification

Gas purification is the treatment of coal gas to remove contaminants such as fly ash, tars, oils, ammonia, and hydrogen sulfide. Some gas streams, while ostensibly being hydrocarbon in nature, may contain large amounts of acid gases such as hydrogen sulfide and carbon dioxide. Most commercial plants employ hydrogenation to convert organic sulfur compounds into hydrogen sulfide. Hydrogenation is effected by means of recycled hydrogen-containing gases or external hydrogen over a nickel molybdate or cobalt molybdate catalyst.

In summary, refinery process gas, in addition to hydrocarbon derivatives, may contain other contaminants, such as carbon oxides (CO_x , where $x = 1$ and/or 2), sulfur oxides (SO_x , where $x = 2$ and/or 3), as well as ammonia (NH_3), mercaptans (R-SH), and carbonyl sulfide (COS).

The presence of these impurities may eliminate some of the sweetening processes, since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes not designed to remove (or incapable of removing) large amounts of acid gases whereas they are capable of removing the acid gas impurities to low levels when the acid gases are present only in low-to-medium concentration in the gas.

The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems. In many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form.

See also: Gas Cleaning.

Gas Streams

The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems. In many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form.

There are many variables in treating gas streams. The precise area of application of a given process is difficult to define, and it is necessary to consider several factors, which are (i) the types of contaminants in the gas stream, (ii) the concentration of each contaminant in the gas stream, (iii) the degree of contaminant removal desired (iv) the selectivity of acid gas removal required, (v) the temperature of the gas stream to be processed, (vi) the pressure of the gas stream to be processed, (vii) the volume of the gas stream to be processed, (viii) the composition of the gas to be processed, (ix) the carbon dioxide-hydrogen sulfide ratio in the gas, and (x) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide (H_2S) and carbon dioxide (CO_2), the gas stream may contain other contaminants, such as mercaptans (RSH) and carbonyl sulfide (COS) (Table G-8). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes are also capable of removing the acid gas impurities to low levels when the acid gases are there in low-to-medium concentrations in the gas.

Table G-8 Nomenclature of relevant properties of the various gas streams*.

Gas	Relevant property
Biogas	Gas produced from a biological source; also referred to as biogas
Blue water gas	Higher heat content (calorific value) gas produced from coal
Casinghead gas	Gas extracted from an oil well by separation at the surface.
Carbureted water gas	Higher heat content (calorific value) gas produced from coal
Coalbed methane	Gas from coal seams
Dry gas	High methane content
High-Btu gas	High energy gas; also called high heat-content gas
Landfill gas	Gas produced by the decay of organic matter in a landfill
Lean gas	High methane content
Low-Btu gas	Low energy gas; also called low heat-content gas
Medium-Btu gas	Medium energy gas; also called medium heat-content gas
Producer gas	Very low heat content (calorific value) gas produced from coal
Residue gas	Gas remaining after the condensing process; predominantly methane
Sour gas	High concentration of hydrogen sulfide (H_2S)
Sweet gas	Low concentration of hydrogen sulfide or no hydrogen sulfide
Synthesis gas	A mixture of carbon monoxide and hydrogen
Wet gas	High concentration of higher-boiling hydrocarbon derivatives (C_5 to C_{10})
Wood gas	Gas produced from wood

*Listed alphabetically.

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream. Gas processing involves the use of several different types of processes, but there is always overlap between the various processing concepts. In addition, the terminology used for gas processing can often be confusing and/or misleading because of the overlap (Nonhebel, 1964; Curry, 1981; Maddox, 1982). There are four general processes used for emission control (often referred to in another, more specific context as flue gas desulfurization: (i) adsorption, (ii) absorption, (iii) catalytic oxidation, and (iv) thermal oxidation (Soud and Takeshita, 1994).

Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. Usually, carbon is the adsorbing medium, which can be regenerated upon desorption. The quantity of material adsorbed is proportional to the surface area of the solid and, consequently, adsorbents are usually granular solids with a large surface area per unit mass. Subsequently, the captured gas can be desorbed with hot air or steam, either for recovery or for thermal destruction.

Adsorbing units (adsorbers) are widely used to increase a low gas concentration prior to incineration unless the gas concentration is high in the inlet air stream. Adsorption also is employed to reduce problem odors from gases. There are several limitations to the use of adsorption systems, but it is generally felt that the major one is the requirement for minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency.

Absorption differs from adsorption, in that it is not a physical-chemical surface phenomenon, but an approach in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (chemisorption). Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, the gas-liquid contactor designs which are employed are plate columns or packed beds.

Absorption is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon). Chemical adsorption processes adsorb sulfur dioxide onto a carbon surface where it is oxidized (by oxygen in the flue gas) and absorbs moisture to give sulfuric acid impregnated into and on the adsorbent. Liquid absorption processes (which usually employ temperatures below 50°C (120°F) are classified either as physical solvent processes or chemical solvent processes. The former processes employ an organic solvent, and absorption is enhanced by low temperatures, or high pressure, or both. Regeneration of the solvent is often accomplished readily. In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkaline solutions such as amines or carbonates. Regeneration (desorption) can be achieved by the use of reduced pressures and/or high temperatures, whereby the acid gases are stripped from the solvent.

Solvents used for emission control processes should have: (i) a high capacity for acid gas, (ii) a low tendency to dissolve hydrogen, (iii) a low tendency to dissolve low-molecular-weight hydrocarbon derivatives, (iv) low vapor pressure at operating temperatures to minimize solvent losses, (v) low viscosity, (vi) low thermal stability, (vii) absence of reactivity toward gas components, (viii) low tendency for fouling, (ix) low tendency for corrosion, and (x) economically acceptable.

Amine washing of gas emissions involves chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat, and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) have been used in commercial applications.

The chemistry can be represented by simple equations for low partial pressures of the acid gases:



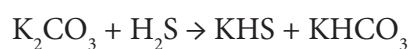
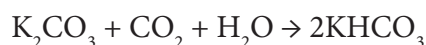
At high acid gas partial pressure, the reactions will lead to the formation of other products:



The reaction is extremely fast, the absorption of hydrogen sulfide being limited only by mass transfer; this is not so for carbon dioxide.

Regeneration of the solution leads to near complete desorption of carbon dioxide and hydrogen sulfide. A comparison between monoethanolamine, diethanolamine, and diisopropanolamine shows that monoethanolamine is the cheapest of the three but shows the highest heat of reaction and corrosion; the reverse is true for diisopropanolamine.

Carbonate washing is a mild alkali process for emission control by the removal of acid gases (such as carbon dioxide and hydrogen sulfide) from gas streams and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature. It has been demonstrated that the process works best near the temperature of reversibility of the reactions:



Water washing, in terms of the outcome, is analogous to washing with potassium carbonate, and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical, and there is also a relatively high absorption of hydrocarbon derivatives, which are liberated at the same time as the acid gases.

In chemical conversion processes, contaminants in gas emissions are converted to compounds that are not objectionable or that can be removed from the stream with greater ease than the original constituents. For example, a number of processes have been developed that remove hydrogen sulfide and sulfur dioxide from gas streams by absorption in an alkaline solution.

Catalytic oxidation is a chemical conversion process that is used predominantly for destruction of volatile organic compounds and carbon monoxide. These systems operate in a temperature regime of 205 to 595°C (400 to 1,100°F) in the presence of a catalyst. Without the catalyst, the system would require higher temperatures. Typically, the catalysts used are a combination of noble metals deposited on a ceramic base in a variety of configurations (e.g., honeycomb-shaped) to enhance good surface contact.

Catalytic systems are usually classified on the basis of bed types such as fixed bed (or packed bed) and fluid bed (fluidized bed). These systems generally have high destruction efficiencies for most volatile organic compounds, resulting in the formation of carbon dioxide, water, and varying amounts of hydrogen chloride (from halogenated hydrocarbon derivatives). The presence in emissions of chemicals such as heavy metals, phosphorus, sulfur, chlorine, and most halogens in the incoming air stream act as poison to the system and can foul up the catalyst.

Thermal oxidation systems, without the use of catalysts, also involve chemical conversion (more correctly, chemical destruction) and operate at temperatures in excess of 815°C (1,500°F), or 220 to 610°C (395 to 1,100°F) higher than catalytic systems.

Historically, particulate matter control (dust control) has been one of the primary concerns of industries, since the emission of particulate matter is readily observed through the deposition of fly ash and soot as well as in impairment of visibility. Differing ranges of control can be achieved by use of various types of equipment. Upon proper characterization of the particulate matter emitted by a specific process, the appropriate piece of equipment can be selected, sized, installed, and performance tested. The general classes of control devices for particulate matter are as follows:

Cyclone collectors are the most common of the inertial collector class. Cyclones are effective in removing coarser fractions of particulate matter. The particle-laden gas stream enters an upper cylindrical section tangentially and proceeds downward through a conical section. Particles migrate by centrifugal force generated by providing a path for the carrier gas to be subjected to a vortex-like spin. The particles are forced to the wall and are removed through a seal at the apex of the inverted cone. A reverse-direction vortex moves upward through the cyclone and discharges through a top center opening. Cyclones are often used as primary collectors because of their relatively low efficiency (50-90% is usual). Some small-diameter high-efficiency cyclones are utilized. The equipment can be arranged either in parallel or in series to both increase efficiency and decrease pressure drop. However, there are disadvantages that must be recognized. These units for particulate matter operate by contacting the particles in the gas stream with a liquid. In principle, the particles are incorporated in a liquid bath or in liquid particles which are much larger and therefore more easily collected.

Fabric filters are typically designed with non-disposable filter bags. As the dusty emissions flow through the filter media (typically cotton, polypropylene, Teflon, or fiberglass), particulate matter is collected on the bag surface as a dust cake. Fabric filters are generally classified on the basis of the filter bag cleaning mechanism employed. Fabric filters operate with collection efficiencies up to 99.9%, although other advantages are evident. There are several issues that arise during use of such equipment.

Wet scrubbers are devices in which a countercurrent spray liquid is used to remove particles from an air stream. Device configurations include plate scrubbers, packed beds, orifice scrubbers, venturi scrubbers, and spray towers, individually or in various combinations. Wet scrubbers can achieve high collection efficiencies at the expense of prohibitive pressure drops.

Other methods include use of high-energy input venturi scrubbers or electrostatic scrubbers where particles or water droplets are charged, and flux force/condensation scrubbers where a hot humid gas is contacted with cooled liquid or where steam is injected into saturated gas. In the latter scrubber, the movement of water vapor toward the cold water surface carries the particles with it (diffusiophoresis), while the condensation of water vapor on the particles causes the particle size to increase, thus facilitating collection of fine particles.

The foam scrubber is a modification of a wet scrubber in which the particle-laden gas is passed through a foam generator, where the gas and particles are enclosed by small bubbles of foam.

Electrostatic precipitators operate on the principle of imparting an electric charge to particles in the incoming air stream, which are then collected on an oppositely charged plate across a high-voltage field. Particles of high resistivity create the most difficulty in collection. Conditioning agents such as sulfur trioxide (SO₃) have been used to lower resistivity.

Important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include the use of high-voltage pulse energy to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations.

See also: Gas Cleaning.

Gas-to-Commodity

The constituents of gas streams all useful in their own right. The higher paraffins are particularly valuable for a wealth of chemicals and polymer precursors such as acetic acid, formaldehyde, olefins, polyethylene, polypropylene, acrylonitrile, ethylene glycol, etc., as well as portable premium fuels, such as propane. In addition, methane can be converted via syngas to methanol, ammonia, syncrude, lubricant, or some precursor for chemicals manufacture, e.g., dimethyl ether (DME), urea, etc., and then used to make chemicals for export.

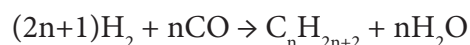
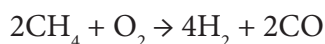
In the gas-to-commodity concept, the gas is converted to thermal or electrical power, which is then used in the production of the commodity, which is then sold, on the open market. It is the energy from the gas, heat via electricity or direct combustion, and not the components of the gas-to-liquids concept that is used. The gas energy is, in essence, transported via the commodity.

Gas-to-Liquids

The gas-to-liquids (GTL) technology involves the conversion of a gas stream (such as, for example, natural gas) to liquid fuels such as gasoline, jet fuel, and diesel fuel. In the process, the Fischer-Tropsch technology is used to combine hydrogen with carbon monoxide to form different liquid hydrocarbon derivatives which are further processed using different refining technologies into liquid fuels.

In gas-to-liquids (GTL) transport process, methane (as the example) is first mixed with steam and converted to syngas (mixtures of carbon monoxide and hydrogen, CO + H₂) by one of a number of routes using suitable new catalyst technology. The syngas is then converted into a liquid using a Fischer-Tropsch process (in the presence of a catalyst) or an oxygenation method (mixing syngas with oxygen in the presence of a suitable catalyst).

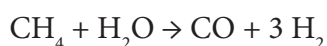
The Fischer-Tropsch process for natural gas involves conversion of methane to mixture of carbon monoxide and hydrogen (synthesis gas) from which hydrocarbon derivatives can be produced by a catalytic process:



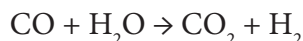
The utility of the process is primarily in its role in producing liquid hydrocarbon derivatives from a carbonaceous feedstock which leads to possible end products including kerosene, naphtha, methanol, dimethyl ether (DME), alcohols, waxes, diesel fuel, and gasoline, with water or carbon dioxide produced as a by-product. Dimethyl ether is also used as a transportation fuel or power generation fuel as well as a chemical feedstock for the petrochemical industry.

Methanol is a gas-to-liquids option that has been in commission since the mid-1940s. While methanol produced from gas was originally a relatively inefficient conversion process, optimized technology has improved the efficiency. Methanol can be used in internal combustion engines as a fuel, but the current market for methanol as a fuel is limited, although the development of fuel cells for motor vehicles may change this. Methanol is best used as a basic chemical feedstock for the manufacture of plastics. Methanol is made from natural gas (methane) in a series of three reactions:

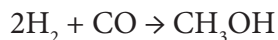
Steam reforming:



Water shift reaction:



Synthesis:



The methanol thus formed may be converted to gasoline by the Mobil process. First methanol is dehydrated to give dimethyl ether:



This is then further dehydrated over a zeolite catalyst, ZSM-5, to give a gasoline with 80% w/w (based on the organics in the product stream) C_{5+} hydrocarbon products. ZSM-5 is deactivated by a carbon build-up over time in converting methanol to gasoline. The catalyst can be re-activated by burning off the coke in a stream of hot [500 °C (930 °F)] air; however, the number of re-activation cycles is limited.

The technology can produce a variety of chemicals and fuels – of particular interest is its ability to yield large volumes of sulfur-free diesel fuel. The process involves reforming natural gas into synthesis gas (also referred to by the shorter name syngas) by combining the gas with steam, air, or oxygen, then converting the synthesis gas-to-liquid hydrocarbon derivatives through catalytic reaction, typically with an iron- or cobalt-based catalyst. The liquid products are hydrocracked and stabilized to create transportation fuels and chemicals.

Until recently, this process has not been competitive in the crude oil marketplace, although it had been used for political reasons in noncompetitive economies. Dramatic recent advances in gas-to-liquids technology focus on improved processes and catalysts, which are reducing costs enough to be more competitive with crude oil-based fuels, depending on gas costs and oil prices.

Gas-to-liquids (GTL) technology mounted on barges or offshore platforms could bring to market liquid transportation fuels from deep-water Gulf of Mexico sites without gas pipeline access. In Alaska, converted gas from the North Slope could be transported through the existing Trans-Alaska Pipeline System (TAPS), from Prudhoe Bay to Valdez, where tankers would deliver these liquids to market.

Fueling vehicles with fuel from a gas-to-liquids process fuel consumes fewer crude oil resources per distance traveled than with a conventional fuel derived from crude oil. In addition, gas-to-liquids technology can exploit biomass in addition to gas reserves and crude oil reserves. Extrapolating from this point, using biomass to create gas-to-liquids fuels will extend the lifetime of natural gas and crude oil reserves accordingly.

See also: Fischer-Tropsch Process, Gasification, Synthesis Gas.

Gas-to-Power

The most common method to generate power from a gas stream (such as natural gas) uses gas turbine generators (GTGs), either in simple-cycle or combined-cycle configurations. Gas-turbine-based power generation has proven to be the lowest-life-cycle-cost alternative to date for large-scale electric power generation from gas streams.

The main energy forecasts identify natural gas as the fastest-growing primary energy source at a global level. As for most other regions of the world, the use of natural gas in power generation is seen as the main driver for this increase. The favorable economics of combined cycle gas turbine (CCGT) power plants, especially their relatively low capital intensity and high conversion efficiencies, make natural gas the fuel of choice for power generation.

Increasing import dependency has reawakened concerns related to security of supply. Another important issue is whether investments in new generating capacity are as high as forecasted. Until recently, prices in many wholesale electricity markets did not appear to justify any substantial new investments in generation plant.

Currently, much of the transported gas destination is fuel for electricity generation. Electricity generation at or near the reservoir source and transportation by cable to the destination(s) (gas-to-power, GTL) is possible.

Thus, for instance, offshore or isolated gas could be used to fuel an offshore power plant (may be sited in less hostile waters), which would generate electricity for sale onshore or to other offshore customers. Unfortunately, installing high-power lines to reach the shoreline appear to be almost as expensive as pipelines, so that gas-to-power could be viewed as defeating the purpose of an alternative cheaper solution for transporting gas. There is significant energy loss from the cables along the long distance transmission lines, more so if the power is AC rather than DC; additionally, losses also occur when the power is converted to DC from AC and when it is converted from the high voltages used in the transmission to the lower values needed by the consumers.

Some consider having the energy as gas that is sent to the consumers gives greater flexibility and better thermal efficiency, because the waste heat can be used for local heating and desalination. This view is strengthened by the economics as power generation uses approximately 1 million scf/day of gas for every 10 MW of power generated, so that even large generation capacity would not consume much of the gas from larger fields, and thus not generate large revenues for the gas producers. Nevertheless, gas-to-power has been an option much considered in the US for getting energy from the Alaskan gas and oil fields to the populated areas.

There are other practical considerations to note such as if the gas is associated gas, then if there is generator shut-down and no other gas outlet, the whole oil production facility might also have to be shut down, or the gas released to flare. Also, if there are operational problems within the generation plant, the generators must be able to shut down quickly (in around 60 s) to keep a small incident from escalating. Additionally, the shutdown system itself must be safe so that any plant that has complicated processes that requires a purge cycle or a cool-down cycle before it can shut down is clearly unsuitable. Finally, if the plant cannot shut down easily and/or be able to start up again quickly (perhaps in an hour), operators will be hesitant to ever shut down the process, for fear of financial retribution from the power distributors.

See also: Turbine.

Gas-to-Solid

Gas can be transported as a solid, with the solid being gas hydrate. Changing natural gas into a hydrate form for cheaper transport gained attention in the early 1990s. Norwegian crude oil engineers first proposed the idea after comparing the transport economics of liquid natural gas to natural gas hydrates, knowing that hydrates could store large amounts of natural gas in a small space – more than 180 standard cubic feet of gas can be stored in one cubic foot of hydrate.

Natural gas hydrate is the product of mixing natural gas with liquid water to form a stable water crystalline ice-like substance. Natural gas hydrate transport is believed to be a viable alternative to liquefied natural gas or pipelines for the transportation of natural gas from source to demand.

Natural gas hydrates are created when natural gas constituents (methane, ethane, and propane) stabilize the physical structure of water to form a three-dimensional cage-like structure with the gas molecule trapped within the cages. A cage is made up of several water molecules held together by hydrogen bonds. The hydrates are formed from natural gas in the presence of liquid water provided the pressure is above and the temperature is below specified limits. The solids have a snow-like appearance and have properties that make them useful in many kinds of applications, including transportation and storage. Gas hydrates contain approximately 15% by weight and 85% by weight water and can contain up to 160 cubic meters of gas per cubic meter of solid hydrate. The exact numbers depend on the gas composition and the formation (production) pressure and temperature.

Vast quantities of gas hydrate have been found in permafrost and at the seabed in depths below 500 m (1,500 ft), and if properly exploited could become a major source of natural gas (therefore, a major energy source) in the next 50 years. On the other hand, natural gas hydrates are a pipeline nuisance and safety hazard, and require considerable care by the operators to ensure that they do not form as they can block pipelines if precautions, such as methanol injection, are not taken.

For gas transportation and/or storage, natural gas hydrates can be deliberately formed by mixing natural gas and water at 1,200 to 1,500 psi and 2 to 10°C. If the slurry is refrigerated to around -15°C, it decomposes very slowly at atmospheric pressure, so that the hydrate can be transported by ship to market in simple insulated under near adiabatic conditions. At the market, the slurry is melted back to gas and water by controlled warming for use after appropriate drying in electricity power generation stations or other requirements. The hydrate mixture yields up to 160 m³

of natural gas per ton of hydrate, depending on the manufacture process. The manufacture of the hydrate could be carried out using mobile equipment for onshore and ship for offshore using a floating production, storage, and offloading vessel with minimal gas processing (cleaning, etc.) prior to hydrate formation, which is attractive commercially.

The water can be used at the destination if there is water shortage, or returned as ballast to the hydrate generator and, since it is saturated with gas, will not take more gas into solution. Process operability of continuous production of hydrate in a large-scale reactor, long-term hydrate storage, and controlled regeneration of gas from storage have all been demonstrated.

The hydrate mixture can be stored at normal temperatures (0 to -10°C) and pressures (10 to 1 atmosphere) where 1 m^3 of hydrate should contain approximately 160 m^3 gas per m^3 of water. This concentration of gas is attractive as it is easier to produce, safer, and cheaper to store compared to the 200 m^3 per 1 m^3 of compressed gas (high pressure ca. 3,000 psig) or the 637 m^3 gas per 1 m^3 of liquefied natural gas (at the low temperatures of -116°C , -177°F).

Gas storage in hydrate form becomes especially efficient at relatively low pressures where substantially more gas per unit volume is contained in the hydrate than in the free state or in the compressed state when the pressure has dropped. When compared to the transportation of natural gas by pipeline or as liquefied natural gas, the hydrate concept has lower capital and operating costs for the movement of quantities of natural gas over adverse conditions. Thus, gas hydrate is effective for gas storage and transport as it eliminates low temperatures and the necessity of compressing the gas to high pressures. Dry hydrate pellets yield approximately 160 m^3 of gas at standard conditions from 1 m^3 of hydrate compared to the 637 m^3 per 1 m^3 of liquefied natural gas. This is a considerable volume penalty (and hence transport cost) if considered in isolation, but by using cheaper ships to transport the hydrate, the process could be economical.

Gas Treating

Gas treating, gas processing, and gas sweetening are terms used to describe the various processes for removal of certain contaminants, primarily hydrogen sulfide and carbon dioxide, from natural gas or hydrocarbon liquids. Other reasons to remove these contaminants include toxicity, corrosiveness, freezing problems, and control of the overall heating value of the natural gas.

Raw natural gas comes primarily from any one of three types of wells: crude oil wells, gas wells, and condensate wells. Natural gas that comes from crude oil wells is typically termed associated gas. This gas can exist separate from the crude oil in the underground formation, or dissolved in the crude oil. Natural gas from gas wells and from condensate wells, in which there is little or no crude oil, is termed non-associated gas. Gas wells typically produce only raw natural gas, while condensate wells produce raw natural gas along with low density liquid hydrocarbon called natural gas condensate (condensate, natural gasoline). Raw natural gas can also come from methane deposits in the pores of coal seams. Such gas is referred to as coalbed gas, and it is also called sweet gas because it is relatively free of hydrogen sulfide.

In addition to hydrogen sulfide and carbon dioxide, the sulfur acids, carbonyl sulfide, carbon disulfide, and the mercaptan family, when present in sufficient quantities, are also candidates for removal with specific amines.

In addition, refinery process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units, and hydroprocessing units can contain high concentrations of hydrogen sulfide mixed with low-boiling refinery fuel gases. Before elemental sulfur can be recovered, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulfide. This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent. Solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbents such as molecular sieves, activated carbon, iron sponge, and zinc oxide are also used. In the amine solvent processes, diethanolamine solution or another amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulfide is dissolved in the solution. The fuel gases are removed for use as fuel in process furnaces in other refinery operations.

There is a number of ways in which to configure the various unit processes used for gas treating. Initially, raw natural gas is commonly collected from a group of adjacent wells and is first processed at that collection point for removal of free liquid water and natural gas condensate. The condensate is usually then transported to an oil refinery and the water is disposed of as wastewater.

The raw gas is then pipelined to a gas treating plant where the initial purification is usually the removal of acid gases (hydrogen sulfide and carbon dioxide). There are many processes that are available for that purpose as shown in the flow diagram, but amine treating (olamine treating) is the process that was historically used. Newer processes,

based on the use of polymeric membranes to separate the carbon dioxide and hydrogen sulfide from the natural gas stream, have gained increasing acceptance.

The acid gases removed by olamine treating or membrane treating can then be routed into a sulfur recovery unit which converts the hydrogen sulfide in the acid gas into either elemental sulfur or sulfuric acid. There is a number of processes available for these conversions, but the Claus process is by far the most well-known for recovering elemental sulfur.

The tail gas from the Claus process is then processed in a tail gas treating unit (TGTU) to recover and recycle residual sulfur-containing compounds back into the Claus unit. Again, as shown in the flow diagram, there are a number of processes available for treating the Claus unit tail gas and for that purpose, a wet sulfuric acid process is also very suitable since it can work autothermal on tail gases.

The next step in the gas processing plant is to remove water vapor from the gas using either the regenerable absorption in liquid triethylene glycol (TEG) (glycol dehydration) or a pressure swing adsorption unit which is regenerable adsorption using a solid adsorbent. Mercury is then removed by using adsorption processes such as activated carbon or regenerable molecular sieves.

Nitrogen is next removed and rejected using one of three processes which are (i) a cryogenic process using low temperature distillation, which can be modified to also recover helium, if desired, (ii) an absorption process using lean oil or a solvent as the absorbent, and (iii) an adsorption process using activated carbon or molecular sieves as the adsorbent. This process may incur the loss of butanes and heavier hydrocarbon derivatives.

The next step is to recover the natural gas liquids (NGL) for which most large, modern gas processing plants use another cryogenic low temperature distillation process involving expansion of the gas through a turbo-expander followed by distillation in a demethanizing fractionating column. Some gas processing plants use lean oil absorption process rather than the cryogenic turbo-expander process.

The residue gas from the section where the natural gas liquids are recovered is the final, purified sales gas, which is pipelined to the end-user markets.

The recovered stream of natural gas liquids is processed through a fractionation train consisting of three distillation towers in series which are (i) a de-ethanizer, which removes ethane, (ii) a depropanizer, which removes propane, and (iii) a debutanizer, which removes butane.

The overhead product from the de-ethanizer is ethane, and the bottoms are fed to the depropanizer. The overhead product from the depropanizer is propane, and the bottoms are fed to the debutanizer. The overhead product from the debutanizer is a mixture of normal and iso-butane, and the bottoms product is a C5+ mixture. The recovered streams of propane, butanes, and C5+ are each sweetened (freed of odiferous sulfur compounds) in a Merox process unit to convert undesirable and odiferous mercaptans (RSH) into disulfides (SSR) and, along with the recovered ethane, are the final natural gas liquids by-products from the gas treating plant.

See also: Gas Cleaning, Gas Processing.

Geochemical Cycles

A developmental path followed by individual elements or groups of elements in the crustal and sub-crustal zones of the Earth and on its surface. The concept encompasses geochemical differentiation (natural separation and concentration of elements) and heat-assisted recombination processes. Changes may not be apparent over a short term, but over a long term, changes of great magnitude occur, including the evolution of continents and oceans. The carbon cycle (Figure G-1) is the geochemical cycle by which carbon is exchanged among the biosphere, exosphere, geosphere, hydrosphere, and atmosphere of the Earth.

The carbon cycle is usually thought of as four major reservoirs of carbon interconnected by pathways of exchange which are (i) plants, (ii) the terrestrial biosphere, which is usually defined to include fresh water systems and non-living organic material, such as soil carbon, (iii) the oceans, including dissolved inorganic carbon and living and non-living marine biota, and (iv) sediments including fossil fuels.

The annual movements of carbon, the carbon exchanges between reservoirs, occur because of various chemical, physical, geological, and biological processes. The ocean contains the largest active pool of carbon near the surface of the Earth, but the deep ocean part of this pool does not rapidly exchange with the atmosphere.

See also: Biogeochemical Cycles.

Geohydrology

Geohydrology (hydrogeology) is the branch of earth science, which deals with the occurrence and movement of subterranean water. It is the subdivision of the science of hydrology that deals with the water beneath the surface of the Earth. It is interdisciplinary in scope in that it involves the application of the physical, biological, and mathematical sciences. Because geohydrology deals with the occurrence and movement of water in an almost infinitely complex subsurface geologic environment, it is, in its most advanced state, one of the most complex of the sciences. On the other hand, many of its basic principles and methods can be understood readily and used in the solution of groundwater problems.

See also: See also: Aquiclude, Aquitard, and Aquifuge; Aquifer.

Geological Age

The Earth is believed to be between 4 and 5 billion years old. Geological age is most commonly measured in millions of years (Table G-9).

Table G-9 Illustration of the age of the earth and the subdivision of the years.

Era	Period	Epoch	Years ago x 10 ⁶ **
Precambrian	Precambrian		570
Paleozoic	Cambrian		510
	Ordovician		439
	Silurian		409
	Devonian		363
	Mississippian*		323
	Pennsylvanian*		290
	Permian		245
Mesozoic	Triassic		208
	Jurassic		146
	Cretaceous		65
Cenozoic	Tertiary	Paleocene	57
		Eocene	35
		Oligocene	23
		Miocene	5
		Pliocene	2
	Quaternary	Pleistocene	0.01
		Holocene	present

*The Mississippian and Pennsylvanian Periods are sometimes (collectively) referred to as the Carboniferous Period. The numbers in years indicate the beginning and the end of the Periods and Epochs.

Geosphere

The geosphere (also called the land systems) constitutes the terrestrial component of the systems of the Earth and encompass all processes and activities related to the human use of land, including, technological and organizational investments and arrangements, as well as the benefits gained from land and the unintended social and ecological outcomes of societal activities. Changes in land systems have large consequences for the local environment and human well-being and are at the same time pervasive factors of global environmental change. In more specific terms, the lithosphere refers to the minerals in the crust of the Earth whereas the term geosphere is often more broad in coverage and refers to the complex and variable mixture of minerals, organic matter, water, and air which make up the soil.

The land provides vital resources to society, such as food and fuel and many other ecosystem services that support production functions, regulate risks of natural hazards, or provide cultural services. By using the land, changes are the direct result of human decision making which range from local land owners decisions to national scale planning and trade agreements. The aggregate impact of many local land system changes has far-reaching consequences for the Earth system, that feedback on ecosystem services, human well-being, and decision making. As a consequence, land system change is both a cause and consequence of socio-ecological processes.

The term Earth system refers to the interacting physical, chemical, and biological processes that occur on the Earth. The system consists of the land, oceans, atmosphere, and poles. It includes the natural cycles of the Earth – the carbon, water, nitrogen, phosphorus, sulfur, and other cycles and deep Earth processes. In addition, life is also an integral part of the Earth system. Life affects the carbon, nitrogen, water, oxygen, and many other cycles and processes. Two other definitions include the terms global change and global climate change.

Global change refers to planetary-scale changes in the Earth system. More completely, the term global change encompasses planetary-scale changes to atmospheric circulation, ocean circulation, climate, the carbon cycle, the nitrogen cycle, the water cycle and other cycles, sea-ice changes, sea-level changes, food webs, biological diversity, pollution, health, fish stocks, and more. Global climate change refers to the long-term average of the aggregation of all components of weather of the components of the climate of the Earth: precipitation, temperature, and cloudiness, for example. The climate system includes processes involving ocean, land, and sea ice in addition to the atmosphere. Many changes in Earth system functioning directly involve changes in climate. However, the Earth system includes other components and processes, biophysical and human, that are important for its functioning. Some Earth system changes, natural or driven by humans, can have significant consequences involving changes in climate.

The lithosphere is outermost shell of the Earth that is composed of the crust and the portion of the upper mantle that behaves elastically on time scales of thousands of years or greater; defined on the mineralogy. The lithosphere is subdivided into tectonic plates which are the uppermost part of the lithosphere that chemically reacts to the atmosphere, the hydrosphere, and the biosphere through the soil-forming process (called the pedosphere) There are two types of lithosphere which are (i) the oceanic lithosphere, which is associated with the oceanic crust and exists in the oceanic basins and has a density of approximately of approximately 2.9 grams per cubic centimeter, and (ii) the continental lithosphere, which is associated with the continental crust and has a on the order of 2.7 grams per cubic centimeter.

The oceanic lithosphere consists mainly of a mafic mantle (mafic: an adjective describing a silicate mineral or igneous rock that is rich in magnesium and iron) crust and ultramafic mantle (over 90% mafic) and is denser than continental lithosphere. It thickens as it ages and moves away from the mid-ocean ridge. This thickening occurs by conductive cooling, which converts hot asthenosphere into lithospheric mantle. It was less dense than the asthenosphere for tens of millions of years, but after this becomes increasingly denser. The gravitational instability of mature oceanic lithosphere has the effect that when tectonic plates come together, oceanic lithosphere invariably sinks underneath the overriding lithosphere. New oceanic lithosphere is constantly being produced at mid-ocean ridges and is recycled back to the mantle at subduction zones, so oceanic lithosphere is much younger than its continental counterpart. The oldest oceanic lithosphere is approximately 170 million years old compared to parts of the continental lithosphere which are billions of years old.

On the other hand, the continental lithosphere (also called the continental crust) is the layer of igneous, sedimentary rock that forms the continents and the continental shelves. This layer consists mostly of granitic rock.

Continental crust is also less dense than oceanic crust, although it is considerably thicker. Approximately 40% of the surface of the Earth is covered by continental crust, but continental crust makes up approximately 70% v/v of the crust of the Earth. The continental crust is believed to have been derived from the fractional differentiation of oceanic crust over geologic time (hundreds of millions of years) and was primarily a result of volcanism and subduction.

The lithosphere is underlain by the asthenosphere, which is the weaker, hotter, and deeper part of the upper mantle. The lithosphere-asthenosphere boundary is defined by a difference in response to stress in which the lithosphere remains rigid for long periods of geologic time in which it deforms elastically and through brittle failure. On the other hand, the asthenosphere undergoes considerable deformation and accommodates strain through this deformation.

The term biosphere refers to living organisms and their environments on the surface of the Earth (Manahan, 1991). Included in the biosphere are all environments capable of sustaining life above, on, and beneath the surface of the Earth as well as in the oceans. Consequently, the biosphere includes virtually all of the water systems (the aquasphere, the hydrosphere) as well as portions of the atmosphere and the upper lithosphere (land systems).

In addition, there are relationships between the atmosphere, the water systems, the land systems, and the biosphere. These relationships are physical and are also caused by environmental forces. It is worth noting here that such relationships, perhaps not in this exact concept, were noted more than four centuries ago. Paracelsus (Philippus Aureolus Theophrastus Bombast von Hohenheim; 1493-1541) taught that the macrocosm (the heavens) and the microcosm (the Earth and all of the living creatures) were linked together and that the macrocosm directed the growth and development of the microcosm.

In the modern relationships between the atmosphere, the water systems, and the land systems, acid rain is the precipitation phenomena that incorporate anthropogenic acids (i.e., those acids which are the result of human activities) and other acidic materials. The deposition of acidic materials into the water systems and onto the land occurs in both wet and dry forms as rain, snow, fog, dry particles, and gases.

The effect of acid rain (acid deposition) on a particular ecosystem depends largely on the sensitivity of the ecosystem to the acid deposition. There is also the ability of the ecosystem to neutralize the acid as well as the concentration and composition of acid reaction products and the amount of acid added to the system.

Trace element is a term that refers to those elements that occur at low levels in a given system. The somewhat ambiguous term probably arose from the inadequacy of earlier analytical techniques – before modern methods such as atomic absorption, plasma emission, neutron-activation analysis, gas chromatography, and mass spectrometry extended the limits of detection to the low levels currently attainable. In many early investigations, it was only possible to detect the presence of an element, as it was said to be present at a trace level. A reasonable definition of a trace element is that the element occurs at a level of a few parts per million or less. The term trace substance is a more general definition that is applied to both elements and chemical compounds.

There are a variety of trace elements encountered in natural waters, some of which are the nutrients required for animal and plant life. Of these, many are essential at low levels but toxic at higher levels. This is typical for many substances in the aquatic environment, a point that must be kept in mind in judging whether a particular element is beneficial or detrimental. Some of these elements, such as lead or mercury, have such toxicological and environmental significance that they are discussed in detail in separate sections.

Some of the heavy metals are among the most harmful of the elemental pollutants. These metals include essential elements like iron as well as toxic metals like lead (Pb), cadmium (Cd), and mercury (Hg). Most of them have a tremendous affinity for sulfur and attack sulfur bonds in enzymes, thus immobilizing the enzymes. Protein carboxylic acid (-COOH) derivatives and amino (-NH₂) groups are also chemically bound by heavy metals. Cadmium, copper, lead, and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate compounds or catalyze their decomposition.

The geosphere includes the parts of Earth where life exists and extends from the deepest root systems of trees, to the dark environment of ocean trenches, to the rain forests and high mountaintops (sometimes referred to as the biosphere). Often, the Earth in terms of spheres – (i) the atmosphere is the layer of air that stretches above the lithosphere, (ii) the water on the surface of the Earth, in the ground, and in the air constitute the hydrosphere, and (iii) the solid surface layer of the Earth is the lithosphere.

An ecosystem is a community of living organisms in conjunction with the nonliving components of their environment (such as air, water, and mineral soil), interacting as a system. Ecosystems are controlled both by (i) external

factors and (ii) internal factors. External factors such as climate, the parent material that forms the soil, and topography control the overall structure of an ecosystem and the way things work within it, but are not themselves influenced by the ecosystem. Internal factors not only control ecosystem processes but are also controlled by them and are often subject to feedback loops. Other internal factors include disturbance, succession, and the types of species present. Although humans exist and operate within ecosystems, their cumulative effects are large enough to influence external factors like climate. An important aspect of the chemistry of the biosphere is the chemistry that occurs in the soil.

The soil itself is a complex mixture of inorganic chemicals – even before pollution occurs. Eight chemical elements comprise the majority of the mineral matter in soils. Of these eight elements, oxygen, a negatively-charged ion (anion) in crystal structures, is the most prevalent on both a weight and volume basis. The next most common elements, all positively-charged ions which, in decreasing order, are silicon, aluminum, iron, magnesium, calcium, sodium, and potassium. Ions of these elements combine in various ratios to form different minerals.

The most chemically active fraction of soils consists of colloidal clays and organic matter. Colloidal particles are so small (<0.0002 mm) that they remain suspended in water and exhibit a large surface area per unit weight. These materials also generally exhibit net negative charge and high adsorptive capacity. Several different silicate clay minerals exist in soils, but all have a layered structure. It is these clay minerals that act as adsorbents for inorganic pollutants (as well as organic pollutants).

The soil transports and moves water, provides refuge for bacteria and other fauna, and has many different arrangements of weathered rock and minerals. When soil and minerals weather over time, the chemical composition of soil also changes. However, many of the problems of soil chemistry problems are concerned with environmental sciences such as the accidental or deliberate disposal of chemicals. This can involve several physical chemical interactions that can cause changes to the soil (i) ion exchange, (ii) soil pH, (iii) sorption and precipitation, and (iv) oxidation-reduction reactions.

Ion exchange involves the movement of cations (positively charged elements such as calcium, magnesium, and sodium) and anions (negatively charged elements such as chloride, and compounds like nitrate) through the soils. More specifically, cation exchange is the interchanging between a cation in the solution of water around the soil particle, and another cation that is on the surface of the clay mineral.

A cation is a positively charged ion and most inorganic contaminants are cations, such as: ammonium (NH_4^+), calcium (Ca^{2+}), copper (Cu^{2+}), magnesium (Mg^{2+}), manganese (Mn^{2+}), potassium (K^+), and zinc (Zn^{2+}). These cations are in the soil solution and are in dynamic equilibrium with the cations adsorbed on the surface of clay and organic matter. It is the cation exchange interaction of ions with clay minerals in the soil that gave soil the ability of soil to adsorb and exchange cations with those in soil solution (water in soil pore space). The adsorption capacity of a clay minerals can cause a mixture of inorganic pollutants to physically transform when one or more constituents of the mixture adsorbs on to a clay mineral. In addition, the total amount of positive charges that the clay can absorb (the cation exchange capacity, CEC) impacts the rate of movement of the pollutants through the soil and the physical and chemical changes that can occur to the pollutants. For example, soil (i.e., clay) with a low cation exchange capacity is much less likely to retain pollutants and, furthermore, the soil (i.e., the clay) is less able to retain inorganic chemicals with the potential that the chemicals are released into the groundwater.

Soil pH is a commonly measured soil chemical property and is also one of the more informative properties since the data imply certain characteristics that might be associated with a soil. For example, the pH of soil is a measure of the acidity or alkalinity: values 0 to 7 indicate acidity, while values from 7 to 14 indicate alkalinity. Typically, the pH value for soil usually ranges from 4 to 10. The pH is an important property that is involved in plant growth, as well as understanding how rapidly reactions occur in the soil. For example, the element iron becomes less available to plants at higher alkalinity ($\text{pH} > 7$) which creates iron deficiency problems. Crops usually have optimal growth at pH values between 5.5 and 8, but the value depends on the crop. The pH of soil also affects the ability of organisms to feed on contaminants. Thus, any chemical spillage on to soil can seriously affect the overall chemistry of the soil and the ability of flora and fauna to survive.

The other principal variables affecting life in soil in the environment include moisture, temperature, and aeration, and the balance of these factors controls the abundance and activities of the floral and faunal inhabitants in the soil which in turn have a marked influence on the critical processes of soil aggregation retention of pollutants.

Soil water is usually derived from rainfall or some other form of overland flow. The amount of water that enters the soil is a function of soil structure which in turn is a function of texture and higher-order structure, i.e., aggregation (e.g., well-aggregated, porous soils allow greater infiltration). Larger pores created by root channels and animal burrows (ant tunnels and worm holes) as well as other types of macropores also greatly facilitate movement of water into and through the soil profile. This is why these soil animals are usually regarded as highly beneficial in soil and why some scientists often use the abundance of earthworms as an indicator of a healthy soil, though it should be remembered that highly fertile, productive soils do not always contain large numbers of earthworms and other soil faunal species.

Although soil is an inorganic matrix of metals and minerals, the main reason why the soil becomes contaminated is due to the presence of anthropogenic waste. This waste is typically (i) chemicals in one form or another that are not indigenous to the soil or (ii) chemicals that are indigenous chemicals that are deposited into the soil in amounts that exceed the natural abundance. The typical actions that lead to pollution of the soil by inorganic chemicals are (i) industrial activities, (ii) agricultural activities, (iii) waste disposal, and (iv) acid rain.

Industrial activities have been the biggest contributor to the soil pollution since the time of the *Industrial revolution*, especially since the amount of mining and manufacturing increased almost logarithmically in the 160 years immediately following 1800. Most industries are dependent on extracting minerals from the Earth, and the by-products have not been sent for disposal in a manner that can be considered safe. Thus, the industrial waste lingers in the soil surface for a long time and makes it unsuitable for use. At the same time, physical changes and chemical changes to the inorganic pollutant also occur for the better or for worse.

Agricultural activities have caused a rise in the use of inorganic chemicals since technology provided the means of producing inorganic pesticides and inorganic fertilizers. They are full of chemicals that are not produced in nature and cannot be broken down by it. These chemicals seep into the ground after they mix with water and slowly change the character of the soil by adsorption and by changing the acidity/alkalinity of the water in the soil. Other chemicals damage the composition of the soil and make it easier to erode by water and air.

Waste disposal has also been major cause for concern insofar as the manner of disposal is subject to scrutiny. While industrial waste is sure to cause contamination. This type of waste typically contains toxins and chemicals which are now seeping into the land and causing pollution of soil. Finally, acid rain is caused when sulfur-containing and nitrogen-containing chemicals present in the air mix up with the rain and fall back to the soil. The polluted (acidified) water has the ability to dissolve away some of the soil constituents and, more drastically, change the structure of the soil. This latter action could release pollutants that were adsorbed (and may have even remained adsorbed) and once released can find their way into groundwater.

Geothermal Energy

Geothermal energy is the heat that comes from the sub-surface of the earth. It is contained in the rocks and fluids beneath the crust of the Earth crust and can be found as far down to the hot molten rock, magma. The internal heat of the Earth is the thermal energy generated from radioactive decay and continual heat loss from formation of the Earth. The slow decay of radioactive particles in the core of the Earth, a process that happens in all rocks, produces geothermal energy. In terms of alternative energy, geothermal energy is the use of the Earth's internal heat for practical purposes and in particular to boil water for heating buildings or generating electricity. Geothermal energy is produced by tapping into the thermal energy created and stored within the earth. It is considered sustainable because that thermal energy is constantly replenished.

The geothermal energy of the crust of the Earth originates from the original formation of the planet (20%) and from the radioactive decay of minerals (80%). The geothermal gradient, which is the difference in temperature between the core of the planet and its surface, drives a continuous conduction of thermal energy in the form of heat from the core to the surface.

By way of explanation, the earth has four major parts or layers: (i) an inner core of solid iron that is approximately 1,500 miles in diameter, (ii) an outer core of hot molten rock called magma that is approximately 1,500 miles thick, (iii) a mantle of magma and rock surrounding the outer core that is approximately 1,800 miles thick, and (iv) a crust of solid rock that forms the continents and ocean floors that is 15 to 35 miles thick under the continents and 3 to

5 miles thick under the oceans, The crust of the Earth is broken into pieces called tectonic plates. Magma comes close to the earth's surface near the edges of these plates, which is where many volcanoes occur. The lava that erupts from volcanoes is partly magma. Rocks and water absorb heat from magma deep underground. The rocks and water found deeper underground have the highest temperatures.

The temperature of the inner core of the Earth is on the order of $6,000^{\circ}\text{C}$ ($10,800^{\circ}\text{F}$), and the temperature at the core-mantle boundary may reach a temperature in excess of $4,000^{\circ}\text{C}$ ($>7,200^{\circ}\text{F}$). The high temperature and pressure in interior of the Earth cause some rocks to melt and the solid mantle to behave plastically, resulting in portions of the mantle flowing upward since it is lighter than the surrounding rock. Rock and water are heated in the crust, sometimes up to 370°C (700°F).

Geothermal thermal energy is used to generate electricity typically via a well that is drilled into an underground reservoir of water that can be as hot as 370°C (700°F). At the surface, a turbine is turned using the trapped steam. Heat pumps are used to move fluids through pipelines buried underground at depths where the temperature does not change much and is delivered to a home or commercial building. During the summer, this pipeline can pull heat out of a building and uses cooler fluid to cool the building. Geothermal water is also found in geysers or hot springs on the surface of the Earth.

To produce power from geothermal energy, wells are dug a mile deep into underground reservoirs to access the steam and hot water there, which can then be used to drive turbines connected to electricity generators. There are three types of geothermal power plants which are (i) dry steam, (ii), flash, and (iii) binary. Dry steam is the oldest form of geothermal technology and takes steam out of the ground and uses it to directly drive a turbine. Flash plants use high-pressure hot water into cool, low-pressure water while binary plants pass hot water through a secondary liquid with a lower boiling point, which turns to vapor to drive the turbine.

Geothermal energy provides a clear, sustainable, environmentally friendly, and substantial resource. However, it also faces challenges in that geothermal plants generally are site-specific and limited to regions with accessible deposits of high temperature ground water; the completion of a geothermal plant takes significant time (four to eight years) versus the times for wind or solar, and there is a lack of transmission lines.

There are many benefits to using geothermal power. It is clean and nonpolluting. It does not require the consumption of fossil fuels, so it reduces dependence on foreign or domestic oil, and it reduces harmful emissions from burning these fuels. Geothermal plants do not destroy large tracts of land. They are efficient: A geothermal plant usually can produce more power than a fossil fuel-burning plant of the same size.

Geothermal plants are also reliable because they do not depend on external fuel sources; they can run twenty-four hours a day, every day of the year. This is not always possible with power plants that burn coal or oil, which must be transported from distant locations. Geothermal plants are not vulnerable to weather, natural disasters, strikes, political disturbances, or other events that can disrupt fuel supplies.

Geothermal plants, on many levels, are flexible. It is possible to build them of modular components and to add or adapt components as the need arises. This is usually not possible with fossil fuel-burning plants. Geothermal power plants are especially valuable in areas with small power grids or in cases where a power grid is in the process of expanding. Flexible geothermal plants can provide backup power while the rest of the grid is installed.

Geothermal energy is generally sustainable and renewable. The Earth generates heat constantly. Rainfall and snowmelt continuously replenish reservoirs, and returning used water to the underground reservoir maintains its pressure and heat so that the reservoir can be used for an indefinite period of time.

The major limitation of geothermal power is that it can only be implemented in areas where there is a ready supply of hot water underground. This limits its use to geologically active areas such as California, Iceland, Japan, and the rest of the Pacific Rim and other areas with a thin crust, an active mantle, and pockets of subterranean hot water. Only the hottest water can be used to generate electricity. Some places have naturally heated groundwater that is not hot enough to produce the steam needed to turn turbines. That water is still usable for other purposes but not as a workable power source.

It is possible to deplete a reservoir. If a geothermal reservoir runs out of water or grows too cool, it ceases to be useful, though this depletion can take decades or even centuries. For this reason, there are claims that geothermal energy is not actually a renewable resource.

Like solar power and wind power, geothermal energy is clean. Geothermal power plants do not have to burn fuels so they do not produce emissions of greenhouse gases or other pollutants, which means they do not contribute to

smog or global warming. They do emit small amounts of carbon dioxide, approximately 4% of the amount emitted by burning fossil fuels. Binary plants produce no emissions at all. Areas that have geothermal power plants tend to have much better air quality than those with fossil fuel-burning power plants.

A geothermal power plant can be small compared to other types of power plants, so it is not as disruptive to the landscape. It can be built right next to its geothermal well. There is no need to build dams, dig mines, cut down trees, or dispose of wastes, which are necessary with other common forms of power. It is actually possible to build geothermal power plants in the middle of farmland or forests without damaging the surrounding plants and animals. Even in areas where geothermal energy is not powerful enough to create electricity, people can still make use of local hot water for heating and bathing. This means they do not have to use electricity from other sources to heat their water, which can help save money and fuel.

There are some minor environmental drawbacks to using geothermal resources. Geothermal reservoirs sometimes contain hydrogen sulfide (H_2S) gas, which smells like rotten eggs and can be toxic at high concentrations. Geothermal power plants use scrubbers to remove this gas from emissions. Geothermal water also contains a high concentration of minerals, so geothermal wells must contain several layers of pipe and casings to prevent geothermal water from mixing with ordinary groundwater. Because geothermal power plants re-inject their used geothermal water back into the underground reservoir, in most cases, the geothermal water never gets near groundwater and cannot harm aquatic plants and animals.

The areas around geothermal power plants experience increased activity, such as small earthquakes, and there is a danger of landslides. Federal laws in the United States prohibit the construction of geothermal power plants in national parks, such as Yellowstone. However, the environmental problems associated with using geothermal energy are generally far less serious than those caused by using fossil fuels.

Geothermal heating has many obvious environmental benefits. It does not pollute the air at all because geothermal heating involves no combustion and therefore no emissions. Geothermal heat pumps pose few environmental problems. They use an antifreeze substance, but it is usually a nontoxic chemical called propylene glycol or small amounts of methanol, both of which are commonly used in windshield washing solutions.

Economically, geothermal heat can be much less expensive than other sources of heat, such as fossil fuels or wood, but that cost depends on several factors. The initial installation costs can be high, but if the heating system works well, it can pay for itself quickly. Geothermal heat works especially well in areas that already have wells dug into geothermal reservoirs. If there are already wells in place, a district or institution only needs to buy pipelines, heat exchangers, and pumps. A heating system is more expensive to install if there is not already a good geothermal reservoir in use.

See also: Geothermal Gradient, Geothermal Power Plants, Radioactive Decay.

Geothermal Energy – Electricity Generation

To produce electricity from a geothermal resource, wells are drilled into the reservoir, and as the hot, high-pressure water travels to surface of the Earth, some of it vaporizes into steam as the pressure decreases. The hotter the original source, the greater the amount of dry steam produced. For dry-steam sources, the technology is basically the same as for electric plants that use the burning of fossil fuels to produce steam, except that the temperature and pressure of the geothermal steam are much lower. Dry-steam fields are being used in the United States, Italy, and Japan. In the Geysers geothermal area in California, the steam temperature is approximately 200°C (390°F) and the pressure on the order of 100 psi.

For geothermal reservoirs that are at lower temperatures, and hence produce less dry steam, working plants usually employ multiple-vaporization systems. The first vaporization (“flash”) is conducted under some pressure, and the remaining pressurized hot water from the ground, along with the hot residual water from the turbine, can be flashed again to lower pressure, providing steam for a second turbine.

If the temperature of the original hot water is too low for effective flashing, the water can still be used to generate electricity in what is referred to as binary cycle (or organic cycle) electricity generation. The hot water is pumped to the surface under pressure to prevent evaporation, which would decrease the temperature, and its heat is transferred to an organic fluid such as isobutane, isopentane, or hexane, all of which have a boiling temperature lower than that

of water. The fluid is vaporized by the heat from the water and acts as the working fluid in a turbine. It has been estimated that geothermal reservoirs with temperatures suitable for binary cycle generation are approximately fifty times as abundant as sources that provide pure dry steam.

Some geothermal power plants use a combination of flash and binary cycles to increase the efficiency of electricity production. An initial flash creates steam that drives a turbine; then, the binary cycle is run, using either the hot water remaining after the initial flash or the hot exhaust from the turbine.

See also: Geothermal Energy, Geothermal Gradient, Geothermal Power Plants.

Geothermal Energy – Environmental Effects

Geothermal power plants are generally environmentally clean. They do not burn fossil fuels, so they help conserve those fuels for other purposes. They produce no emissions to contribute to air pollution, the greenhouse effect, or global climate change. There is no smoke surrounding geothermal power plants. Dry steam and flashed steam plants emit excess steam and small amounts of gases, while binary plants emit nothing at all because all the fluids are contained within the system and recycled.

Geothermal plants do not need space to store fuels, and they do not create large piles of ash that must be cleared or oil spills that damage oceans. They also do not pollute groundwater unless the geothermal water has a high concentration of minerals or metals. Unlike most other power plant types, geothermal plants do not require large amounts of space to function. They can be built right on top of geothermal reservoirs. The pumps that bring water up from geothermal reservoirs are small, especially compared to those used by coal mines or oil wells. They do not tear up large plots of land or destroy forests. There is no need to build major highways, railroads, or pipelines in order to transport fuel to geothermal power plants because their source of power is directly below them. It is actually possible to build geothermal power plants in the midst of farmland or forests, where they can coexist with livestock and wildlife.

The most important potential environmental impacts of geothermal energy are water and air pollution. At the largest geothermal plants, thousands of tons of hot water and/or steam are extracted per hour, and these fluids contain a variety of dissolved pollutants. The hot geothermal water dissolves salts from surrounding rocks, and this salt produces severe corrosion and scale deposits in equipment. To prevent contamination of surface water, the geothermal brine must either be returned to its source or discarded carefully in another area. In addition to salts, the geothermal waters sometimes contain high concentrations of toxic elements such as arsenic, boron, lead, and mercury.

Geothermal water often contains dissolved gases as well as salts and toxic elements. One of the gases that is often found in association with geothermal water and steam is hydrogen sulfide, which is toxic in high concentrations.

Geothermal brines also are a source of the greenhouse gas carbon dioxide, which contributes to global climate change. However, a typical geothermal electrical plant produces only approximately 5% of the carbon dioxide emitted by a fossil-fuel-fired plant generating the same amount of electricity. Many modern geothermal plants can capture the carbon dioxide (as well as the hydrogen sulfide) and reinject it into the geothermal source along with the used geothermal fluids. At these facilities, the carbon dioxide that escapes into the atmosphere is less than 0.1% of the emissions from a coal- or oil-fired plant of the same capacity.

Another potential problem, particularly if geothermal water is not returned to its source, is land subsidence. For example, there may be significant subsidence and another annoying difficulty with geothermal heat has been the noise produced by escaping steam and water. The shriek of the high-pressure fluids is intolerable, and is usually dissipated in towers in which the fluids are forced to swirl around and lose their kinetic energy to friction. However, the towers provide only partial relief, and the plants are still noisy.

See also: Gas Cleaning, Geothermal Energy, Geothermal Power Plants.

Geothermal Gradient

The geothermal gradient is the rate of increase in temperature per unit depth in the Earth. It varies with location and is typically measured by determining the bottom open-hole temperature after borehole drilling.

For example, crude oil in an underground formation is much more fluid than it is on the surface and is generally mobile under reservoir conditions because the elevated temperatures (the geothermal gradient) in subterranean formations decrease the viscosity. Although the geothermal gradient varies from place to place, it is generally on the order of 25 to 30°C/km (15°F/1,000 ft or 120°C/1,000 ft, i.e., 0.015°C per foot of depth or 0.012°C per foot of depth).

In the geosciences, the measurement of temperature (T) is associated with heat flow (Q):

$$Q = K\Delta T/\Delta Z$$

K is the thermal conductivity of the rock.

Temperatures at the surface of the earth are controlled by the Sun and the atmosphere, except for areas such as hot springs and lava flows. From shallow depths to approximately 200 ft below the surface, the temperature is constant at approximately 11°C (55°F). In a zone between the near surface and approximately 400 feet (122 meters), the gradient is variable because it is affected by atmospheric changes and circulating groundwater. Below that zone, temperature almost always increases with depth. However, the rate of increase with depth (geothermal gradient) varies considerably with both tectonic setting and the thermal properties of the rock.

High gradients (up to 11°F/100 ft, or 200°C/km) are observed along the oceanic spreading centers (for example, the Mid-Atlantic Rift) and along island arcs (for example, the Aleutian chain). The high rates are due to molten volcanic rock (magma) rising to the surface. Low gradients are observed in tectonic subduction zones because of thrusting of cold, water-filled sediments beneath an existing crust. The tectonically stable shield areas and sedimentary basins have average gradients that typically vary from 0.82 to 1.65°F/100 ft (15 to 30°C/km).

The geothermal gradient is important for the oil, gas, and geothermal energy industries. Downhole logging tools must be hardened if they are to function in deep oil and gas wells in areas of high gradient. Calculation of geothermal gradients in the geological past is a critical part of modeling the generation of hydrocarbon derivatives in sedimentary basins.

See also: Geothermal Energy, Geothermal Power Plants.

Geothermal Heat Pumps

Geothermal heat pumps work by pumping water or a mix of water and antifreeze through the ground next to a house or building. The ground temperature remains relatively constant throughout the year, generally between 7 and 12°C (45 and 55°F). In winter, 7 and 12°C underground pipes absorb heat from the Earth. This heated water circulates into the heat pump, where it is concentrated so that it will increase to the desired room temperature. The heat pump then pumps the hot air through the ducts in the building, heating the rooms. In summer, the process is reversed; the hot air is sucked from the building and dispersed into the ground. The geothermal heat pump system uses ordinary ductwork, so there is no need to modify existing ducts.

Geothermal heat pumps usually can at least partially heat water for the home. This is not necessarily possible all year round. During the summer, the heat pump can use excess heat to warm domestic hot water, but during the winter, there is not as much heat available to warm the water. A home with a geothermal heat pump must usually have an alternate source of heat for water, but even so, using excess heat for even part of the year results in an energy savings. New technology is improving this situation; because geothermal heat pumps are so much more efficient than other forms of water heating, some manufacturers are now selling geothermal heat pumps that heat water separately, thereby providing hot water year-round.

Geothermal heat pumps, like all heat pumps, produce slightly warmer air than fossil fuel furnaces. Geothermal heat pumps generally produce hot air between 35 and 39°C (95 and 103°F), as opposed to conventional heat pumps, which produce hot air between 32 and 35°C (90 and 97°F). Geothermal heat pumps require more open ductwork for air flow than fossil fuel furnaces, which can be a problem when converting older houses to geothermal heat.

See also: Geothermal Energy, Geothermal Gradient.

Geothermal Power Plants

One very promising use of geothermal power is the generation of electricity. Areas with hot geothermal reservoirs can use this heat and steam to create electricity without having to spend money for fuel and without polluting the atmosphere or ground.

Geothermal power plants are similar to other steam turbine thermal power stations in that heat from a fuel source (in the case of geothermal energy, from the core of the Earth) is used to heat water or another working fluid. The working fluid is then used to turn a turbine of a generator, thereby producing electricity.

Geothermal power plants are usually built with modular designs, which makes them very flexible. It is easy to start with a small plant and then add additional units if the demand for electricity increases. Geothermal plants can also use some of their water, either freshly pumped or after being used for electricity, for other direct purposes, such as heating or aquaculture.

However, not every location can use geothermal power. Geothermal power plants must be located near a geothermal reservoir that has water of at least 121°C (250°F) and preferably 150°C (300°F). Not all reservoirs have water this hot. An ideal geothermal reservoir is hot with low mineral content, has shallow aquifers nearby to make it easy to re-inject used water, is on private land in order to make it easier to get permits, is near existing electrical transmission lines, and has a supply of cooler water for cooling. It also needs a high enough volume of water to keep flowing steadily.

In terms of the operation of a geothermal power plant, all types of geothermal power plants use geothermal steam to turn a turbine. The turbine is attached to a generator that creates the electricity. The electricity is then fed into a grid, which is attached to individual users. There are three main types of geothermal power plant: binary, dry steam, and flashed steam. There are also hybrid power plants that combine geothermal energy with other energy sources. The type of plant built in a given area depends on what sort of geothermal resource is available, either steam or liquid and either high or low temperature.

Binary Power Plants

In these binary cycle plants, the main difference is that the water or steam from below the earth never comes in direct contact with the turbines. Instead, water from geothermal reservoirs is pumped through a heat exchanger where it heats a second liquid which boils at a lower temperature than water. This second liquid is heated into steam, which powers the turbines that drives a generator. The hot water from the earth is recycled into the earth through the injection well, and the second liquid is recycled through the turbine and back into the heat exchanger where it can be used again.

Thus, binary power plants use a two-step process to extract power from geothermal water that is not quite hot enough to spin a turbine by itself. The hot water is pumped up through the ground and passed through a heat exchanger that contains a fluid with a much lower boiling point than water. The heat from the geothermal water causes this “binary” fluid to flash into vapor. That vapor spins the turbine, which powers the generator. The geothermal water is injected back into the reservoir. The binary fluid stays inside the tank, where it is used over and over again. Nothing is released into the atmosphere.

Many areas have geothermal reservoirs with water that is below 205°C (400°F). Moderate-temperature geothermal water is much more common than high-temperature water.

Closed Loop Power Plant

Closed loop horizontal power plant systems are the most cost-effective for residential areas. For larger commercial buildings, closed loop vertical systems are more often used. These can sometimes go down 400 feet deep.

In a closed loop system, a water/antifreeze mixture circulates through a loop of pipes underground (or beneath a body of water) and into a building. In the winter (as shown above), the temperatures underground are warmer than the air, so the fluid pumping in is warmer. Then the electric compressors and heat exchangers transfer the heat through ducts in the building. In the summer, the pipes draw heat away from the building and it is absorbed into the earth or water.

Dry Steam Power Plants

Dry steam power plants use the steam that comes up from a geothermal reservoir to power turbines that power generators. Dry steam plants are the most common types of geothermal power plants, accounting for about half of the installed geothermal plants. They work by piping hot steam from underground reservoirs directly into turbines from geothermal reservoirs, which power the generators to provide electricity. After powering the turbines, the steam condenses into water and is piped back into the earth via the injection well.

Flash Steam Power Plants

Flash steam power plants are the most common type of geothermal power plant. This type of power plant differs from the dry steam power plant because hot water, rather than steam, is pumped directly to the surface. The hot water from below the earth into a flash tank on the surface and is at a high pressure.

The fluid is pumped up at high pressure and then sprayed into a tank that is at lower pressure than the water. This causes the geothermal water to “flash,” or turn into steam instantly. The steam spins a turbine, which powers a generator. Fluid left in the first tank is then pumped into another tank to be flashed again. After the water has been used, it is injected back into the reservoir to regain its heat.

Hybrid Power Plants

Some areas do not have enough geothermal energy to run a full power plant. These places can be ideal sites for hybrid power plants that combine different types of power generation. They can combine different types of geothermal energy generation or combine geothermal energy with other energy sources, even fossil fuels.

Open Loop Power Plants

In open loop power plant systems, the water is taken directly from a water source and into the heat pump where it then can either be recycled back into the same source or pumped into another water source (without polluting). The only difference with the water going in and out is a slight change in temperature. Although these systems can be cheaper, they also require a steady flow of water capable of powering your home.

See also: Geothermal Energy, Steam Turbine.

Geothermal Sources

Geothermal sources are categorized into various types which are (i) hydrothermal reservoirs, (ii) geopressurized zones, (iii) hot dry rock, (iv) normal geothermal gradient, and (v) magma.

Hydrothermal Reservoirs

Groundwater can seep down along faults in the crust of the Earth and become heated through contact with hot rocks below. Sometimes, this hot water accumulates in an interconnected system of fractures and becomes a hydrothermal reservoir. The water might remain underground or might rise by convection through fractures to the surface, producing geysers and hot springs.

Hydrothermal reservoirs are the only geothermal sources that have been used for commercial energy production. Because of the high pressure deep below Earth's surface, the water in these sources can become heated well above the usual boiling temperature of 100°C (212°F). As the superheated water makes its way to the surface, either by convection or because a geothermal well has been drilled, some or all of the water will vaporize to become steam because of the lower pressures encountered. The most desirable geothermal sources have high temperatures – above 300°C (570°F) – and all of the water vaporizes to produce dry steam (containing no liquid water), which can be used directly in steam-electric turbines.

Wet steam reservoirs are much more common than the simple dry type. Again, the field is full of hot water, under such high pressure that it cannot boil. When a lower-pressure escape route is provided by drilling, some of the water suddenly evaporates (flashes) to steam, and it is a steam-water mixture that reaches the surface. The steam can be used to drive a turbine. The hot water also can be used to drive a second turbine in a binary cycle. Many geothermal reservoirs contain hot water at a temperature too low for electricity generation. However, the water can be used to

heat buildings such as homes, greenhouses, and fish hatcheries. This heating can be either direct or through the use of heat pumps.

Geopressurized Zones

Geopressurized zones are regions where water from an ancient ocean or lake is trapped in place by impermeable layers of rock. The water is heated to temperatures between 100°C (212°F) and 200°C (390°C) by the normal flow of heat from Earth's core, and because of the overlying rock, the water is held under high pressure. Thus, energy is contained in the water because of both the temperature and the pressure, and can be used to generate electricity. Many geopressurized zones also contain additional energy in the form of methane from the decay of organic material that once lived in the water. The U.S. Geological Survey has estimated that approximately one-third of the energy from geopressurized zones in the United States is available as methane.

Hot Dry Rock

In many regions of the world, hot rocks lie near surface of the Earth, but there is little surrounding water. Attempts have been made to fracture such rocks and then pump water into them to extract the thermal energy, but the technical difficulties in fracturing the rocks have proven to be much more troublesome than anticipated, and there has been a problem with water losses. Consequently, progress in extracting energy from hot, dry rocks has been slow. However, experiments are ongoing in the United States, Japan, and Europe because the amount of energy available from hot, dry rocks is much greater than that from hydrothermal resources.

Normal Geothermal Gradient

In principle, the normal geothermal gradient produces a useful temperature difference anywhere on the globe. If a hole is drilled to a depth of 6 kilometers (which is feasible), a temperature difference of approximately 180°C (325°F) is available, but no technology has been developed to take advantage of this resource. At this depth, water is unlikely, and the problems of extracting the energy are similar to the difficulties encountered with hot, dry rocks near the surface.

Magma

Magma is subterranean molten rock, and although the potential thermal resource represented by magma pools and volcanoes is extremely large, it also presents an immense technological challenge. The high temperatures produce obvious problems with melting and deformation of equipment. The most promising candidates for heat extraction from magma are young volcanic calderas (less than a few million years old) that have magma relatively close to the surface. The hope is that heat can be extracted in this area by drilling a well down to the magma level and pumping water into the well to solidify the magma at the bottom of the well. Then, more water could be pumped into the well, become heated by contact with the solidified magma, and then returned to the surface to generate steam for electricity production.

See also: Geothermal Energy.

Giant Reed Grass

Giant reed grass (Spanish cane, wild cane or giant cane, *Arundo donax*) is a wild plant growing in southern Europe regions. Although giant reed grass grows best in a warm climate, certain genotypes can be adapted to cooler climates and can be grown in countries like Germany or the United Kingdom.

Giant reed grass is a perennial that grows in dense clumps, 5 to 20 feet tall. The leaves can be 1 to 2 feet long and from 1 to 2 inches wide at the base and appear alternate on the stem and point straight out. Stems are 1/2 to 1+ inches in diameter and are hollow, resembling bamboo. The roots are tough and fibrous and, along with extensive rhizomes, form knotty, spreading mats that penetrate deep into the soil. The flower heads are borne in a large (up to feet) plume-like terminal panicles. Seed production is low, and those that do form are considered sterile. In nature, giant reed is primarily vegetatively propagated by rhizomes or viable nodes of mature cane.

Giant Reed is one of the most productive crops as its yield reaches more than 12 tons per acre of dry matter as well as one of the most cost-effective energy crops because it is perennial with low annual inputs after establishment of the crop. The annual input consists of harvesting, irrigation, and/or fertilization costs. Giant reed is one of the largest grass species that can be grown in cool temperatures, and it can grow up to 5 meters tall and 3.5 cm in diameter. Giant Reed is usually harvested either in autumn or in a late winter. Though harvesting in late winter can result in losses of the crop yield (leaves and tops are usually lost). Depending on its use, it is either harvested each year or every second year.

Processing of giant reed grass into biofuel may involve gasification and subsequent conversion to synthetic biofuel or conversion into cellulose-ethanol by sequential treatments involving pretreatment, saccharification, and fermentation.

See also: Biomass.

Girbotol Process

The Girbotol process is a continuous, regenerative process to separate hydrogen sulfide, carbon dioxide, and other acid impurities from natural gas, refinery gas, etc., using mono-, di-, or triethanolamine as the reagent.

The process uses an aqueous solution of ethanolamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

See also: Gas Cleaning, Gas Cleaning – Chemisorption, Gas Processing.

Girdler Process

The Girdler process is an amine (olamine) washing of natural gas to remove acid gases and involves chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat, and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) have been used in commercial applications.

Amine washing of gas emissions involves chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat, and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) have been used in commercial applications.

The chemistry can be represented by simple equations for low partial pressures of the acid gases:



At high acid gas partial pressure, the reactions will lead to the formation of other products:



The reaction is extremely fast, the absorption of hydrogen sulfide being limited only by mass transfer; this is not so for carbon dioxide.

Regeneration of the solution leads to near complete desorption of carbon dioxide and hydrogen sulfide. A comparison between monoethanolamine, diethanolamine, and diisopropanolamine shows that monoethanolamine is the cheapest of the three but shows the highest heat of reaction and corrosion; the reverse is true for diisopropanolamine.

One key difference among the various specialty amines is selectivity toward hydrogen sulfide; instead of removing both hydrogen sulfide and carbon dioxide, as generic amines such as MEA and DEA do, some products readily remove hydrogen sulfide to specifications, but allow controlled amounts of carbon dioxide to slip through. When the methyl diethanolamine process was developed in the mid-1970s, it was principally destined for the sweetening of gases which did not require complete carbon dioxide removal, or required the removal of only a controlled part of the carbon dioxide. The selectivity of methyl diethanolamine based products can lead to more energy savings. For example, allowing carbon dioxide to remain in the treated gas reduces the amount of acid gas in the amine that needs to be regenerated, thus reducing the amount of energy required.

A series of chemical activators used with methyl diethanolamine offers the most cost-effective answer to complete or controlled acid gas removal from sour to very sour natural gases. However, there are limitations of even the most advanced activated methyl diethanolamine only-based gas treatment technologies in handling very highly acid gas-loaded natural or associated oil field gases, especially for bulk acid gas removal when the acid gases are destined for cycling and/or disposal by re-injection. The activated methyl diethanolamine process is probably the most cost-effective solution to meet the widest range of applications from complete carbon dioxide removal to bulk hydrogen sulfide and/or carbon dioxide removal even for acid gas re-injection projects.

The general process flow diagram for an amine sweetening plant varies little, regardless of the aqueous amine solution used as the sweetening agent. The sour gas containing hydrogen sulfide and/or carbon dioxide will nearly always enter the plant through an inlet separator (scrubber) to remove any free liquids and/or entrained solids. The sour gas then enters the bottom of the absorber column and flows upward through the absorber in intimate counter-current contact with the aqueous amine solution, where the amine absorbs acid gas constituents from the gas stream. Sweetened gas leaving the top of the absorber passes through an outlet separator and then flows to a dehydration unit (and compression unit, if necessary) before being considered ready for sale.

In many units, the rich amine solution is sent from the bottom of the absorber to a flash tank to recover hydrocarbon derivatives that may have dissolved or condensed in the amine solution in the absorber. The rich solvent is then preheated before entering the top of the stripper column. The amine-amine heat exchanger serves as heat conservation device and lowers total heat requirements for the process. A part of the absorbed acid gases will be flashed from the heated rich solution on the top tray of the stripper. The remainder of the rich solution flows downward through the stripper in countercurrent contact with vapor generated in the reboiler. The reboiler vapor (primarily steam) strips the acid gases from the rich solution. The acid gases and the steam leave the top of the stripper and pass overhead through a condenser, where the major portion of the steam is condensed and cooled. The acid gases are separated in the separator and sent to the flare or to processing. The condensed steam is returned to the top of the stripper as reflux.

Lean amine solution from the bottom of the stripper column is pumped through an amine-amine heat exchanger and then through a cooler before being introduced to the top of the absorber column. The amine cooler serves to lower the lean amine temperature to the 100°F range. Higher temperatures of the lean amine solution will result in excessive amine losses through vaporization and also lower acid gas carrying capacity in the solution because of temperature effects.

Diethanolamine (DEA) has a higher boiling temperature than monoethanolamine, requiring other methods of reclaiming such as vacuum distillation in order to prevent thermal degradation of the amine. Moreover, diethanolamine has a slow degradation rate. Consequently, in most cases, it is not practical, economical, or necessary to reclaim DEA solutions. Solution purification is maintained by mechanical and carbon filtration, and by caustic or soda ash addition to the system to neutralize the heat-stable amine salts.

Moisture may be removed from hydrocarbon gases at the same time as hydrogen sulfide is removed. Moisture removal is necessary to prevent harm to anhydrous catalysts and to prevent the formation of hydrocarbon hydrates (such as the propane hydrate, $C_3H_8 \cdot 18H_2O$) at low temperatures. A widely used dehydration and desulfurization process is the glycol/amine process, in which the treatment solution is a mixture of ethanolamine and a large amount

of glycol. The mixture is circulated through an absorber and a reactivator in the same way as ethanolamine is circulated in the Girbotol process. The glycol absorbs moisture from the hydrocarbon gas passing up the absorber; the ethanolamine absorbs hydrogen sulfide and carbon dioxide. The treated gas leaves the top of the absorber; the spent ethanolamine glycol mixture enters the reactivator tower, where heat drives off the absorbed acid gases and water.

The processes using ethanolamine and potassium phosphate are now widely used. The ethanolamine process, known as the Girbotol process, removes acid gases (hydrogen sulfide and carbon dioxide) from liquid hydrocarbon derivatives as well as from natural and from refinery gases. The Girbotol treatment solution is an aqueous solution of ethanolamine, which is an organic alkali that has the reversible property of reacting with hydrogen sulfide under cool conditions and releasing hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

Global Climate Change

The environment is in a state of continual change, and not only as a result of modern activities. In fact, ever since life first appeared, the atmosphere has been influenced by the metabolic processes of living organisms. Of which humans have probably caused the greatest changes even though the human tenure on the Earth has been the shortest relative to the terms of other (floral and faunal) species.

Global climate change (often referred to as global warming or global environmental change) is an emotional environmental issue that deals with the potential for global climate change due to increased levels of atmospheric greenhouse gases.

There are many anthropogenic activities which emit a variety of atmospheric contaminants including sulfur dioxide, particulate matter, photochemically reactive hydrocarbon derivatives, chlorofluorocarbon derivatives, and chemicals (such as those that contain toxic heavy metals). These activities include the use (combustion) of fossil fuels which can introduce carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen oxides, hydrocarbon derivatives (including methane), particulate soot, polynuclear aromatic hydrocarbon derivatives, and fly ash into the atmosphere.

Global warming is the increase in the average temperature of the near-surface air and oceans of the Earth since the mid-20th century and its projected continuation. It has been concluded that increasing greenhouse gas concentrations resulting from human activity such as fossil fuel burning and deforestation are responsible for the observed temperature increase since the middle of the 20th century. However, natural phenomena such as solar variation, volcanoes, and the existence of an interglacial period (inter-ice-age period when the Earth will warm) produce most of the warming. These basic facts are often omitted by the global warming proponents, while the opponents deny any contribution from anthropogenic activities. Climate model projections are often based on the fallacy of either view point as well as the failure to recognize the contributions from all sources.

The most commonly cited indication of global warming is the trend in globally averaged temperature near the surface of the Earth which, expressed as a linear trend, show alarming increases in temperature, even though some recent winters have been reminiscent of an ice age.

The issues remain emotional and political, and the mis-use of data and statistics has hurt both proponents and opponents of the theory.

See also: Climate Change.

Glycol-Amine Gas Treating

Glycol-amine treating is a continuous, regenerative process to simultaneously dehydrate and remove acid gases from natural gas or refinery gas. The primary process for sweetening sour natural gas is quite similar to the processes of

glycol dehydration and natural gas liquids absorption. In this case, however, amine solutions are used to remove the hydrogen sulfide. This process is known simply as the amine process (olamine process) or alternatively as the Girdler process, and is used in the majority of gas sweetening operations.

In the process, the sour gas is run through a tower, which contains the amine solution. This solution has an affinity for sulfur, and absorbs it much like glycol absorbing water. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. Like the process for natural gas liquids, extraction and glycol dehydration, the amine solution used can be regenerated (that is, the absorbed sulfur is removed), allowing it to be reused to treat more sour gas.

Although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponges to remove the sulfide and carbon dioxide.

See also Gas Cleaning, Gas Processing, Glycol-Based Processes.

Glycol-Based Processes

Absorption dehydration involves the use of a liquid desiccant to remove water vapor from the gas. Although many liquids possess the ability to absorb water from gas, the liquid that is most desirable to use for commercial dehydration purposes should possess the following properties: (i) high absorption efficiency, (ii) relatively easy and economic regeneration, (iii) non-corrosive and non-toxic, (iv) no operational problems when used in high concentrations, and (v) no interaction with the hydrocarbon portion of the gas, and no contamination by acid gases.

Glycols are the most widely used absorption liquids as they approximate the properties that meet the commercial application criteria. The glycol derivatives, particularly ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol are the most appropriate for satisfying these criteria to varying degrees. Water and the glycols show complete mutual solubility in the liquid phase due to hydrogen-oxygen bonds, and their water vapor pressures are very low. A frequently used process is the triethylene glycol (TEG) process. In those situations where inhibition is not feasible or practical, dehydration must be used. Both liquid and solid desiccants may be used, but economics frequently favor liquid desiccant dehydration when it will meet the required dehydration specification.

In the process, wet natural gas first enters an inlet separator to remove all liquid hydrocarbon derivatives from the gas stream. Then, the gas flows to an absorber (contactor) where it is contacted countercurrently and dried by the lean triethylene glycol. However, the triethylene glycol also absorbs volatile organic compounds (VOCs) that vaporize with the water in the reboiler. Dry natural gas exiting the absorber passes through a gas/glycol heat exchanger, and then into the sales line. The wet (rich) glycol exiting the absorber flows through a coil in the accumulator where it is preheated by hot lean glycol. After the glycol-glycol heat exchanger, the rich glycol enters the stripping column and flows down the packed bed section into the reboiler. Steam generated in the reboiler strips absorbed water and volatile organic compounds out of the glycol as it rises up the packed bed. The water vapor and desorbed natural gas are vented from the top of the stripper. The hot regenerated lean glycol flows out of the reboiler into the accumulator (surge tank) where it is cooled via cross exchange with returning rich glycol; it is pumped to a glycol/gas heat exchanger and back to the top of the absorber.

Glycol derivatives are typically used for applications where dew point depressions of the order of 15 to 49°C (59 to 120°F) are required. Diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TREG) are used as liquid desiccants, but TEG is the most common for natural gas dehydration.

In the triethylene glycol process, wet gas first enters an inlet separator to remove all liquid hydrocarbon derivatives from the gas stream after which the gas flows to an absorber (contactor) where it is contacted countercurrently and dried by the lean triethylene glycol. The triethylene glycol also absorbs volatile organic compounds (VOCs) that vaporize with the water in the reboiler. The dry natural gas exiting the absorber passes through a gas/glycol heat exchanger and then into the sales line. The wet or rich triethylene glycol exiting the absorber flows through a coil in the accumulator where it is preheated by hot lean glycol. After the glycol-glycol heat exchanger, the rich glycol enters the stripping column and flows down the packed bed section into the reboiler. Steam generated in the reboiler strips absorbed water and volatile organic compounds out of the glycol as it rises up the packed bed, and the water vapor

and desorbed natural gas are vented from the top of the stripper. The hot regenerated lean triethylene glycol flows out of the reboiler into the accumulator (surge tank) where it is cooled via cross exchange with returning rich glycol; it is pumped to a glycol/gas heat exchanger and back to the top of the absorber.

Generally, the contact between a wet gas and glycol can be made in any gas-liquid contact device and is predominantly an absorption/stripping type process, similar to the oil absorption process. The wet gas is dehydrated in the absorber, and the stripping column regenerates the water-free triethylene glycol. The glycol stream should be recharged constantly because some triethylene glycol may react and form higher-molecular-weight products which should be removed by the filter shown or by distillation of a slip stream.

A distinct difference between the chemical-based (e.g., glycol absorption) and the non-chemical-based (e.g., adsorption) dehydration techniques is that the chemical-based techniques will saturate the gas with chemicals at operational conditions. Both techniques can in principle remove almost all the water from the gas, but the phase behavior of the natural gas leaving the processes will be different. Even though chemicals used for absorption in general will have low vapor pressure and relatively small amounts will condense per cubic meter gas, the effect of condensation has to be considered in design of pipelines and process equipment.

The glycol derivative has a chemical affinity for water and removes water from the gas stream. In this process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. Essentially, glycol dehydration involves using a glycol solution, usually either diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in a *contactor*. The glycol solution will absorb water from the wet gas, and once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The natural gas, having been stripped of most of its water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100°C, 212°F) and glycol (204°C, 400°F) makes it relatively easy to remove water from the glycol solution, allowing it to be reused in the dehydration process.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In the past, this methane was simply vented out of the boiler. In addition to losing a portion of the natural gas that was extracted, this venting contributes to air pollution and the greenhouse effect. In order to decrease the amount of methane and other compounds that are lost, flash tank separator-condensers work to remove these compounds before the glycol solution reaches the boiler. Essentially, a flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbon derivatives to vaporize (*flash*). The glycol solution then travels to the boiler, which may also be fitted with air- or water-cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas (e.g., higher-molecular-weight hydrocarbon vapors, the Drizo process) or vacuum distillation are recommended.

See also: Gas Cleaning.

Glycol Degradation

Glycol degradation is caused primarily by either oxidation or thermal degradation. Glycol readily oxidizes to form corrosive acids. Oxygen can enter the system with incoming gas, from unprotected storage tanks or sumps, and through packing glands. Although oxidation inhibitors (such as a 50-50 blend of monoethanolamine (MEA) and 33% hydrazine solution) can be used to minimize corrosion, a better approach to controlling oxidation is blanketing the glycol with natural gas, which can be applied to the headspace in storage tanks and any other area where glycol may contact oxygen. Thermal degradation of the glycol results from the following conditions: high reboiler temperature, high heat flux rate, and localized overheating. The reboiler temperature should always be kept below 400°F to prevent degradation, and a good fire tube design should inherently prevent a high heat flux rate. Localized overheating can be caused by deposits of salts or hydrocarbon derivatives. In addition, thermal degradation of the glycol produces acidic degradation products that lower the pH and increase the rate of degradation, creating a destructive cycle.

Glycol Dehydration

Natural gas from the well is usually saturated with water which in the presence of methane at low temperature can form hydrates, which are solids which will block pipes and valves and stop the operation of the plant.

Among the different gas drying processes, absorption is the most common technique, where the water vapor in the gas stream becomes dissolved in a liquid solvent stream. Glycols are the most widely used absorption liquids as they approximate the properties that meet the commercial application criteria. Several glycols have been found suitable for commercial application. The commonly available glycols and their uses are described as follows:

1. Monoethylene glycol (MEG); high vapor equilibrium with gas so tend to lose to gas phase in contactor. Use as hydrate inhibitor where it can be recovered from gas by separation at temperatures below 50°F.
2. Diethylene glycol (DEG); high vapor pressure leads to high losses in contactor. Low decomposition temperature requires low reconcentrator temperature (157 to 170°C, 315 to 340°F) and thus cannot get pure enough for most applications.
3. Triethylene glycol (TEG); most common. Reconcentrate at 170 to 205°C (340 to 400°F) for high purity. At contactor temperatures in excess of 50°C (120°F) tends to have high vapor losses to gas. Dew point depressions up to 67°C (150°F) are possible with stripping gas.
4. Tetraethylene glycol (TREG); more expensive than TEG but less loss at high gas contact temperatures. Reconcentrate at 400 to 430 °F.

Triethylene glycol is by far the most common liquid desiccant used in natural gas dehydration. It exhibits most of the desirable criteria of commercial suitability:

1. Triethylene glycol is more easily regenerated to a concentration of 98-99 % in an atmospheric stripper because of its high boiling point and decomposition temperature.
2. Triethylene glycol has an initial theoretical decomposition temperature of 207°C (404°F), while that of diethylene glycol is only 164°C (328°F).
3. Vaporization losses are lower than monoethylene glycol or diethylene glycol.
4. Triethylene glycol is not too viscous above 21°C (70°F).

Ethylene glycol is injected into the gas upstream of the plant, where it combines with any free water. After the water is separated from the gas and natural gas liquids, the water is put through a reboiler where the glycol boils off and is recycled for re-use.

The glycol plant is often the least stable component of a gas system and requires the most operator attention. A glycol contacting column (with the gas flowing up through glycol coming down) can also be used to provide a more efficient process and is usually a better option if NGLs are to be transported with the gas in the pipeline in two-phase flow.

Some systems use methanol for drying the gas. The methanol is injected upstream of the cooling process where it combines with the water. The methanol is later recovered from the liquid water/methanol mixture by stripping with a slip stream of the feed gas in a stripper column. Pure water is recovered from the bottom of the column, and the methanol saturated stream from the top is recirculated back into the main gas stream.

In a typical triethylene glycol dehydration process, water-saturated gas enters near the bottom of the contactor tower and flows upwards through the internal trays/packing. Lean glycol enters the contactor tower near the top and cascades down through the contactor making contact with the up-flowing gas stream. The countercurrent flow path of the glycol and the high contact surface area adsorbs water into the glycol from the gas stream. Dehydrated gas flows out of the top of the contactor, while the rich glycol flows out of the bottom of the contactor and to the glycol regeneration section.

The glycol regeneration process typically involves passing the rich glycol through the still column to gain some heat before entering the flash drum. The glycol is then passed through particle filters to remove particulates and activated carbon filters to remove any dissolved hydrocarbon and/or chemical compounds. The rich glycol is heated in a cross exchanger to preheat the feed to the still column where the glycol present in the water vapor leaving the reboiler is recovered.

Depending on the application, it may be necessary to increase the lean glycol concentration by using stripping gas, or running the reboiler/still column under a slight vacuum. Lean glycol (typically >99% w/w purity) is then cooled and pumped back to the top of the contactor tower to repeat the process.

(See also: Gas Cleaning, Gas Processing.)

Gobar Gas

Gobar gas is biogas generated out of cow dung. In India, Gobar gas is generated at the countless number of micro plants (an estimated more than 2 million) attached to households. The Gobar gas plant is basically an airtight circular pit made of concrete with a pipe connection.

Gobar gas production is an anaerobic process and is carried out in an airtight, closed cylindrical concrete tank (digester). The tank has a concrete inlet basin on one side for feeding fresh cattle dung (gobar). There is a concrete outlet on the outer side for removing the digested sludge. The top of the tank serves as the gas tank. It has an outlet pipe for the gobar gas.

In the process, fresh cattle dung is mixed with equal amount of water, and fed daily into the digester tank through the inlet and allowed to remain there. Gobar gas collects in the space above the slurry in the main tank. It is conducted through the outlet pipe and used for domestic purposes. The digested sludge (digested biomass) is automatically removed from the tank through and is an excellent fertilizer.

The degree of digestion of the gobar from the beginning to the end is determined by the ambient temperature. If the temperature is not high enough, then all the gobar is not digested and so there is less gas and the output slurry is not as rich in nitrogen and so is not such a good fertilizer. Anyway, that is the price in these cold climates.

See also: Anaerobic Digestion, Biogas, Digesters.

Grain Crops

Grain crops include corn, wheat, rice, barley, and other cereals. The seeds of these plants are typified by their high starch content that can be hydrolyzed to fermentable sugars for ethanol production. The sugar crops, including sugar cane, beet, and sweet sorghum, are preferable to the starch crops to the extent that sucrose is more readily hydrolyzed to fermentable sugars. However, sugar cane production is restricted to warm climates, and requires both high-quality land and irrigation.

Sugar beets produce only 40% as much fermentable sugar as does sugar cane per unit growing area, and reportedly have a higher value as cattle feed than as an energy feedstock. Sweet sorghum is currently a minor crop in the United States, but has considerable advantages over sugar cane as an energy crop. It can grow in a variety of soils and climatic conditions, and its production costs have been estimated to be just over half those for sugar cane.

A most important factor that arises in considering the use of cropland for energy is the competition with the food market. There is no assurance that cropland will in the future be available in the United States for energy uses, and the cultivation of specific energy crops may have to be limited to avoid inflation of food prices.

Crop residues do not have the high starch or sugar content of the crop itself, but are essentially lignocellulosic materials. As in the case of grasses, crop residues are probably more suited to gasification or direct combustion. Processes for the conversion of cellulosic biomass to ethanol are, however, being investigated and may prove viable.

See also: Crops Residue, Crops.

Grasses

Grasses are usually herbaceous plants with narrow leaves growing from the base. They include the true grasses of the Poaceae (or Gramineae) family, as well as the sedges (Cyperaceae) and the rushes (Juncaceae).

The true grasses include cereals, bamboo, and the grasses of lawns (turf) and grassland. Sedges include many wild marsh and grassland plants, and some cultivated ones such as water chestnut (*Eleocharis dulcis*) and papyrus sedge (*Cyperus papyrus*).

Most of the interest in grass biomass tends to focus on economics, but there is a list of traits that should be considered and valued when evaluating a potential solid biomass energy source. These traits are beneficial to society in general, or impact the suitability of biomass for a farm operation.

See also: Reed Canary Grass, Sorghum.

Grassland Pasture and Range

All open land used primarily for pasture and grazing, including shrub and brush land types of pasture; grazing land with sagebrush and scattered mesquite; and all tame and native grasses, legumes, and other forage used for pasture or grazing; because of the diversity in vegetative composition, grassland pasture and range are not always clearly distinguishable from other types of pasture and range; at one extreme, permanent grassland may merge with cropland pasture, or grassland may often be found in transitional areas with forested grazing land.

Grease Car

A grease car is a diesel-powered automobile rigged postproduction to run on used vegetable oil.

In an effort to reduce dependency on crude oil-based fuels, there is an interest in installing conversion kits which allow diesel engines to burn waste vegetable oil along with standard diesel or biodiesel fuel.

A grease car uses filtered vegetable oil, often obtained at little to no cost from local restaurants, to power a slightly modified diesel engine. The primary modifications made to a grease car are a new storage tank for the vegetable oil, additional fuel filters, and a heater to bring the oil up to operating temperature.

A grease car gets approximately the same mileage as a regular diesel car, and the emission levels are a marked improvement over other types of vehicles, making it a phenomenal tool for reducing pollution. Greenhouse gas emissions can drop anywhere from 78 to 87% overall when you convert a diesel car to a grease car. While they still emit nitrogen oxides and carbon monoxide, grease cars are carbon-neutral.

A grease car may also require standard diesel fuel during the start-up process since the vegetable oil may not readily ignite at lower air temperatures until warmed by a heater unit.

One difficulty grease car owners face is a regular supply of suitable vegetable oil, and the owner of such a vehicle should first negotiate with local restaurants and other food establishments to pick up their waste oil for free. In addition, the oil must also be filtered, which means investing in a commercial filtering system or creating one from scratch.

See also: Biodiesel, Vegetable Oil.

Grease Trap

A grease trap consists of a small tank or chamber which slows the speed of product or effluent flow. In the grease trap, fats, oils, and grease float to the top of the water phase and form a layer of scum (sometimes referred to as sludge) that is contained within the tank. This can then be removed and disposed of as chemical waste or be recognized as a potentially useful product. Relatively clean water exits from the grease trap for disposal.

See also: Chemical Waste, Sludge, water.

Greenhouse Effect

The greenhouse effect is the rise in temperature that the Earth experiences because certain gases in the atmosphere (for example: water vapor, carbon dioxide, nitrous oxide, and methane) trap energy from the sun.

The amount of heat energy added to the atmosphere by the greenhouse effect is controlled by the concentration of greenhouse gases in the atmosphere of the Earth. All of the major greenhouse gases have increased in concentration since the beginning of the Industrial Revolution (approximately 1700 AD). As a result of these higher concentrations, scientists

predict that the greenhouse effect will be enhanced and the climate of the Earth will become warmer. Predicting the amount of warming is accomplished by computer modeling. Computer models suggest that a doubling of the concentration of the main greenhouse gas, carbon dioxide, may raise the average global temperature between 1 and 3° Celsius.

However, the numeric equations of computer models do not accurately simulate the effects of a number of possible negative feedbacks. For example, many of the models cannot properly simulate the negative effects that increased cloud cover would have on the radiation balance of a warmer Earth. Increasing the temperature of the Earth would cause the oceans to evaporate greater amounts of water, causing the atmosphere to become cloudier. These extra clouds would then reflect a greater proportion of the energy of the Sun back into space reducing the amount of solar radiation absorbed by the atmosphere and the surface of the Earth. With less solar energy being absorbed at the surface, the effects of an enhanced greenhouse effect may be counteracted.

A number of gases are involved in the human-caused enhancement of the greenhouse effect and include carbon dioxide (CO_2); methane (CH_4); nitrous oxide (N_2O); chlorofluorocarbons (CF_xCl_x); and tropospheric ozone (O_3). Of these gases, the single most important gas is carbon dioxide which accounts for approximately 55% of the change in the intensity of the greenhouse effect.

See also: Greenhouse Gases.

Greenhouse Gases

Greenhouse gases are chemical compounds that contribute to the greenhouse effect. When in the atmosphere, a greenhouse gas allows sunlight (solar radiation) to enter the atmosphere where it warms the surface of the Earth and is reradiated back into the atmosphere as longer-wave energy (heat). Greenhouse gases absorb this heat and trap it in the lower atmosphere. The two major greenhouse gases are water vapor and carbon dioxide. Other greenhouse gases include methane, ozone, chlorofluorocarbons, and nitrous oxide.

Some greenhouse gases such as carbon dioxide occur naturally and are emitted to the atmosphere through natural processes and human activities. Other greenhouse gases (e.g., fluorinated gases) are created and emitted solely through human activities. The principal greenhouse gases that enter the atmosphere because of human activities are carbon dioxide, methane, nitrous oxide, and fluorinated gases.

Carbon dioxide enters the atmosphere through the burning of fossil fuels (oil, natural gas, and coal), solid waste, trees, and wood products, and also as a result of other chemical reactions (e.g., manufacture of cement). Carbon dioxide is also removed from the atmosphere when it is absorbed by plants as part of the biological carbon cycle.

Methane is emitted during the production and transport of coal, natural gas, and oil. Methane emissions also result from livestock and other agricultural practices and by the decay of organic waste in municipal solid waste landfills.

Nitrous oxide is emitted during agricultural and industrial activities, as well as during combustion of fossil fuels and solid waste.

Hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride are synthetic, powerful greenhouse gases that are emitted from a variety of industrial processes. Fluorinated gases are sometimes used as substitutes for ozone-depleting substances (i.e., chlorofluorocarbons, hydrochlorofluorocarbons, and halons). These gases are typically emitted in smaller quantities, but because they are potent greenhouse gases, they are sometimes referred to as high global warming potential gases (high GWP gases).

Greenhouse gases vary in their ability to absorb and hold heat in the atmosphere (greenhouse effect). Hydrofluorocarbons and perfluorocarbons are the most heat-absorbent, but there are also wide differences between naturally occurring gases. For example, nitrous oxide absorbs 270 times more heat per molecule than carbon dioxide, and methane absorbs 21 times more heat per molecule than carbon dioxide.

See also: Greenhouse Effect.

Greenhouse Gas Production

Greenhouse gas production associated with lignocellulosic-based feedstocks is anticipated to be much lower than with conventional fuels. The environmental performance depends very much on the specific life cycle of the fuel,

including the country in which the life cycle assessment (LCA) was conducted, the feedstock on which the fuel is based, the vehicle used, the propulsion system, and the overall state of technology.

In general, fuels (and chemicals) made from lignocellulosic materials are characterized by reduced carbon dioxide emissions when compared to similar products derived from crude oil. Most biofuels can reduce greenhouse gas emissions significantly and substituting emissions by utilizing bio-based energy can create an overall negative emission for the fuel.

Fischer-Tropsch (F-T) fuels based on bio-residues are likely to have the lowest possible emissions; this is typical of diesel propulsion systems that have better energy recovery. If energy crops are utilized as a feedstock, the overall emissions rise slightly, because the benefit of residue disposal is lost. Ethanol from residues or from energy crops also have relatively low emissions, particularly compared to conventional fuels including gasoline and diesel fuel.

For ethanol from lignocellulose, there is a potential to reduce greenhouse gas emissions with improved technology. This reflects the close-to-commercial status of the technology and the anticipated improvements that will be seen as this technology improves.

See also: Biorefinery.

Gross Sample

For analytical purposes, there should be a sampling plan which typically involves three steps which are (i) physically removing the sample from the material – i.e., the target material or target population, (ii) preserving the sample, and (iii) preparing the sample for analysis. Except for in situ sampling, a sample is analyzed after removing it from its target material and because sampling exposes the target material to potential contamination, the sampling device must be inert and clean.

After removing a sample from the target material, there is a possibility (depending upon the chemical properties and the physical properties of the material) that it will undergo a chemical or physical change (as a result of chemical processes, biological processes, or physical processes) before the analysis can be completed. If such a change occurs, the properties of the sample no longer are representative of the target material population. To circumvent such a problem, any sample taken in the field must be preserved (protected) before transporting the samples to the laboratory for analysis. Even when analyzing samples in the field, preservation may still be necessary. After preserving a sample, it may be safely stored for later analysis. The maximum holding time between preservation and analysis depends on the stability of the sample and the effectiveness of sample preservation.

The initial sample taken from the target material is the gross sample, and may be (i) a single increment drawn from the target material or (ii) a composite of several increments. In many cases, the gross sample cannot be analyzed without first reducing the size of the sample and converting the sample into a more readily analyzable form, or improving the homogeneity of the sample. While this is particularly true for solid sample, liquids and gaseous sample may stratify in the storage container and, therefore not be the presentative sample that is desired.

Furthermore, unlike gases and liquids, a solid sample usually needs some processing before analysis because the standard deviation for sampling is a function of the number of particles in the sample, not the combined mass of the particles. For a heterogeneous material consisting of large particles, the gross sample may be too large to analyze. Reducing the average particle size in the sample allows the analysts to collect the same number of particles with a smaller, more manageable mass.

Reducing the particle size is accomplished by a combination of crushing and grinding the gross sample. The resulting particles are then thoroughly mixed and divided into sub-samples of smaller mass. However, this process may not occur in a single step and the sub-samples may require recycling through the crushing and grinding process several times until a final laboratory sample is obtained.

Thus, a gross sample of a feedstock or product is a sample that represents a quantity, or increment, of a larger quantity of the material to be analyzed and is composed of a number of increments on which neither reduction nor division has been performed. More specifically, the samples chosen for analysis are often called sampling increments or sampling units. In summary, the collection of sampling units or increments is called the gross sample. For laboratory analysis, the gross sample is usually reduced in size and homogenized to create the laboratory sample and the method of obtaining a laboratory sample can be represented simply as follows:

Identify/collect the material → collect a gross sample → reduce to a laboratory sample

The goals of the sampling process are: (i) to obtain a sample that is representative of the total material to be analyzed and which is representative (i.e., an unbiased estimate of the whole sample) – this goal can be realized only if all parts of the material to be analyzed have an equal probability of being included in the sample, and (ii) to obtain a variance in the measured analyte concentration that is an unbiased estimate of the material so that valid confidence limits can be found for the mean – this goal can be reached only if every possible sample is equally likely to be drawn. Both goals require obtaining a random sample – a randomization procedure may be used wherein the samples taken from the material are assigned a number, and then a sample to be tested is selected from a table of random numbers.

Ideally, the gross sample is a miniature replica of the entire mass of material to be analyzed. It is the collection of individual sampling units and must be representative of the whole in composition and in particle-size distribution. The size of the gross sample is determined by (i) the uncertainty that can be tolerated between the composition of the gross sample and that of the whole material, (ii) the degree of heterogeneity of the whole, and (iii) for solid material, the level of particle size at which heterogeneity begins. Specifically, the composition of the gross sample and the laboratory sample must closely resemble (in fact, be a replica of) the average composition of the total mass of material to be analyzed.

The mineral matter content of the feedstock (often incorrectly designated as ash content since there is no ash in, for example, raw biomass feedstocks) is the property most often used in evaluating sampling procedures. Environmentally, sulfur content has also been applied in the evaluation of sampling procedures.

Groundwater

Groundwater is a vital resource that plays a crucial role in geochemical processes, such as the formation of secondary minerals. Groundwater is the part of the hydrosphere most vulnerable to damage from chemical wastes and fuels (conventional or unconventional) that are inadvertently spilled on to the surface of the Earth. The nature, quality, and mobility of groundwater are all strongly dependent upon the rock formations in which the water is held.

Groundwater in nature occurs in two different zones: (i) an unsaturated zone, and (ii) a saturated zone. The unsaturated zone occurs immediately below the land surface in most areas and contains both water and air. In the unsaturated zone, flow occurs beneath the land surface and above the groundwater table. The groundwater table forms the boundary between unsaturated subsurface flow (above it) and saturated subsurface flow (below it). In the unsaturated zone, the preferred path of movement of moisture is vertical, by percolation, toward the saturated zone. Water in the saturated zone is the only water under the surface that is available to supply wells and springs and is the only water to which the name groundwater is correctly applied. Recharge of the saturated zone occurs by percolation of water from the land surface through the unsaturated zone. The water table is the level in the saturated zone at which the hydraulic pressure is equal to the atmospheric pressure and is represented by the water table. Below the water table, the hydraulic pressure increases with increasing depth. In the saturated zone, the preferred path of movement of moisture is horizontal, toward aquifer discharge areas.

Although surface water supplies are subject to contamination, groundwater can become almost irreversibly contaminated by the improper land disposal of chemicals and fuels. Once there is penetration into aquatic systems, chemical species are subject to a number of chemical and biochemical processes. These include acid-base, oxidation-reduction, precipitation-dissolution, and hydrolysis reactions, as well as biodegradation.

Under many circumstances, biochemical processes largely determine the fates of chemical species in water. The most important such processes are those mediated by microorganisms. In particular, the oxidation of biodegradable organic wastes in water generally occurs by means of microorganism-mediated biochemical reactions. Bacteria produce organic acids and chelating agents, such as citrate, which have the effect of solubilizing heavy metal ions. Some mobile methylated forms, such as compounds of methylated arsenic and mercury, are produced by bacterial action.

Physically, an important characteristic of such formations is their porosity, which determines the percentage of rock volume available to contain water. A second important physical characteristic is permeability, which describes

the ease of flow of the water through the rock. High permeability is usually associated with high porosity. However, clays tend to have low permeability even when a large percentage of the volume is filled with water.

Most groundwater originates from precipitation in the form of rain or snow. Water from precipitation that is not lost by evaporation, transpiration, or to stream runoff, may infiltrate into the ground. Initial amounts of water from precipitation onto dry soil held very tightly as a film on the surfaces and in the micropores of soil particles. At intermediate levels, the soil particles are covered with films of water, but air is still present in larger voids in the soil. The region in which such water is held is called the unsaturated zone or zone of aeration, and the water present in it is vadose water. At lower depths, in the presence of adequate amounts of water, all voids are filled to produce a zone of saturation, the upper level of which is the water table.

Groundwater is in constant motion from a point of recharge to a point of discharge in accordance with the laws governing flow of fluids in porous media. The law of linear resistance gives the rate at which groundwater in motion loses energy. Further, because of addition and withdrawal from storage, the volume of groundwater in motion changes with distance according to the principle of conservation of mass. In general, this can be expressed through equation of continuity:

$$\text{Mass inflow rate} = \text{mass outflow rate} + \text{change of mass storage with time}$$

The rate of movement of groundwater depends on the type of subsurface rock materials in a given area. Saturated permeable formations like sands, gravel, weathered/fractured, or structurally deformed hard rocks are a favorable medium for groundwater flow. Impermeable formations such as clay minerals, shale, fines, silts, and solid hard rocks do not offer or favor easy groundwater flow.

In areas where groundwater is used faster than it is naturally replenished, groundwater shortage is faced for small periods or continually depending upon the recharge rate. The categorization of areas for groundwater development suggests four categories: (i) safe, (ii) semi critical, (iii) critical, and (iv) over-exploited. The stage is defined as the ratio of the existing groundwater draft to the net annual groundwater availability. The net annual groundwater availability has been defined as the estimated resource minus a certain allowance for the natural groundwater discharge.

In certain areas, groundwater is polluted by natural processes and the groundwater is contaminated with minerals such as like fluoride, arsenic, and nitrate; groundwater can be polluted by industrial effluents, landfills, septic tanks, leaky underground pipelines, and from overuse of fertilizers and pesticides. When groundwater becomes polluted, it will no longer be safe to drink. The majority of the population in India is in the urban areas, and almost everyone who lives in rural areas uses groundwater for drinking water. The largest use for groundwater is to irrigate crops.

See also: Groundwater Aquifer.

Groundwater Aquifer

A groundwater aquifer is an underground layer of a water-bearing permeable rock, a rock fracture, or unconsolidated material such as gravel, sand, or silt from which the water can be extracted by means of a well. The terms related to aquifer are (i) aquitard, which is a bed of low permeability along an aquifer and (ii) aquiclude or aquifuge, which is a solid, impermeable area underlying or overlying an aquifer, the pressure of which could create a confined aquifer.

As a source of sustainable drinking water, a groundwater aquifer normally requires a means of recharging. Most groundwater aquifers are replenished via rivers or rain. This water may seep into the groundwater aquifer as groundwater flow through the soil. Sometimes, an aquifer may fill up during a rainy season, and then gradually dry out during the summer.

The depth at which a groundwater aquifer is found in a particular geographic region usually depends on the level of the water table in the area. The water table refers to the depth under the ground at which the pressure of groundwater is equal to the pressure of the atmosphere, and usually is regarded as the top level of accessible groundwater in a given area. The water table depth changes with time, and there may be a significant difference in the water table depth from season to season, which can affect the depth at which local groundwater aquifers are accessible.

See also: Aquiclude, Aquitard, and Aquifuge, Groundwater.

Growing Stock

The forests of the world fulfill many roles such as (i) providing renewable raw materials and energy, (ii) maintaining biodiversity, and (iii) protecting land and water resources. However, they can be damaged by fire, agricultural and urban expansion, and other disturbances.

Forests influence climate change by affecting the amount of carbon dioxide in the atmosphere by removing carbon dioxide from the atmosphere by absorption in the wood, the leaves, and the soil. Because forests can absorb and store carbon over an extended period of time, they are often labeled as carbon sinks. This carbon remains stored in the forest ecosystem but can be released into the atmosphere when forests are burned. Quantifying the substantial roles of forests in absorbing, storing, and releasing carbon is key to understanding the global carbon cycle and hence climate change.

Growing stock is a measure of the volume of stem-wood in an area of forest or wooded land and provides information on existing wood resources but also a basis for estimating the amount of carbon contained. Overall, growing stock has been decreasing slightly with some regional differences: Africa, Asia, and South America show a slight decrease, while Europe as well as North and Central America show a slight increase. The term carbon stock refers to the amount of carbon stored in the forest ecosystems of the world, predominantly in living biomass and soil but to a lesser extent also in dead wood and litter.

Thus, growing stock is a classification of timber inventory that includes live trees of commercial species meeting specified standards of quality or vigor; cull trees are excluded. The term growing stock volume refers to the above-stump volume of living trees measured from the bark up to the treetops. It includes all living trees, the diameter of which at breast height (dbh. – or 4 feet) is over 0 cm. It is the living tree component of the standing volume, which also includes dead trees.

The average annual mortality of growing stock is the average cubic foot volume of sound wood in growing-stock trees that died in one year. This statistic is an average for the years between inventories. Growing stock data provide not only information on existing wood resources but also a basis for estimating the amount of carbon contained.

Guard Bed

A guard bed is a bed of an adsorbent (such as, for example, bauxite) that protects a catalyst bed by adsorbing species detrimental to the catalyst. Catalyst bed fouling is present to some degree in, for example, hydrotreating units. When fouling begins to affect hydrotreater cycle length, it is necessary to employ guard bed catalysts to protect valuable downstream catalyst.

The foulants that cause problems in a hydrotreater come from several different sources. The primary foulants are in the feed, or are generated in the equipment upstream of the hydrotreater or even in the hydrotreater itself. These foulants fall into three different categories which are (i) particulates of widely varying size and composition, (ii) reactive molecules such as olefin derivatives and oxygenate derivatives, and (iii) inorganic chemical poisons such as arsenic, nickel, iron, vanadium, and silicon.

The solution is a graded system of guard bed catalysts to balance the deposition and storage of particulates at different layers in the catalyst bed.

The guard bed can be made up of any suitable adsorbing material, which has (i) high adsorption capacity, insofar as the material is porous and has a high surface area, (ii) high selectivity for the contaminants, (iii) structures stable to chemical or thermal attack, and (iv) regenerability at typical regeneration conditions.

Suitable guard bed materials are dependent upon the material to be removed and include activated charcoal, or a siliceous material including clay, silica, silica gel, silica-alumina, and zeolite. Siliceous material of high adsorption capacity as exhibited by a surface area of 1 to 1,000 m² per gram, preferably 10 to 500 m² per gram is preferable. Another approach entails the use of an adsorbent of slight acidity, a strong acidity being undesirable owing to the difficult regeneration of strongly adsorbed organic bases. The zeolites can be partially ion-exchanged and in the hydrogen form to adjust their acidity.

Guard Bed Reactor

Feedstocks that have relatively high content of metals (>300 ppm) substantially increase catalyst consumption because the metals poison the catalyst, thereby requiring frequent catalyst replacement. The usual desulfurization catalysts are relatively expensive for these consumption rates, but there are catalysts that are relatively inexpensive and can be used in the first reactor to remove a large percentage of the metals. Subsequent reactors downstream of the first reactor would use normal hydrodesulfurization catalysts. Since the catalyst materials are proprietary, it is not possible to identify them here. However, it is understood that such catalysts contain little or no metal promoters, i.e., nickel, cobalt, and molybdenum. Metals removal on the order of 90% has been observed with these materials.

Thus, one method of controlling demetallization is to employ separate smaller guard reactors just ahead of the fixed-bed hydrodesulfurization reactor section. The preheated feed and hydrogen pass through the guard reactors that are filled with an appropriate catalyst for demetallization that is often the same as the catalyst used in the hydrodesulfurization section. The advantage of this system is that it enables replacement of the most contaminated catalyst (guard bed), where pressure drop is highest, without having to replace the entire inventory or shut down the unit. The feedstock is alternated between guard reactors while catalyst in the idle guard reactor is being replaced.

When the expanded-bed design is used, the first reactor could employ a low-cost catalyst (5% of the cost of Co/Mo catalyst) to remove the metals and subsequent reactors can use the more selective hydrodesulfurization catalyst. The demetallization catalyst can be added continuously without taking the reactor out of service, and the spent demetallization catalyst can be loaded to more than 30% vanadium, which makes it a valuable source of vanadium.

Gum

An insoluble tacky semi-solid material formed as a result of the storage instability and/or the thermal instability of fuels from a variety of sources.

Gasoline and diesel fuel are susceptible to formation of insoluble gum upon exposure to atmospheric oxygen. During storage, gum formation is particularly severe in fuels derived from catalytic refining processes. Gum formation in gasoline is the result of oxidation and polymerization of unsaturated components, particularly dienes or highly unsaturated compounds, the resulting product being resinous gums. Similarly, diesel fuels form gums during storage. Some types of gums are soluble in the fuel, and a residue is formed after the fuel has been evaporated. Thus, a buildup of gum can form on the fuel injection system. Moreover, insoluble solid particles can form when stocks containing dissolved gums are blended together. The particles can clog fuel filters and injection systems. When motor fuels are stored for any considerable period, an additive to inhibit oxidative gum formation is incorporated into the fuel.

Gum content is influenced by the age of the fuel and its exposure to oxygen and certain metals such as copper. If the fuel (such as gasoline) is allowed to evaporate, the residue left can form gum and varnish. It is important for the fuel to contain as little gum residue as possible to prevent gum formation. Some fuels contain additives made up of aromatic amines and phenols to prevent formation of gum and varnish. During storage, harmful gum deposits may form due to the reaction of some fuel components with each other and with oxygen. Oxidation inhibitors are added to promote fuel stability and control gum and deposit formation. In aviation turbine fuels, large quantities of gum show contamination of fuel by higher boiling oils or particulate matter. A high existent gum content generally reflects poor handling practices in distribution downstream of the refinery.

Gum Formation

Gum formation (ASTM D525, IP 40) alludes to the formation of soluble organic material, whereas sediment is the insoluble organic material. Storage stability (or storage instability) (ASTM D381, ASTM D4625, IP 131, IP 378) is a term used to describe the ability of the liquid to remain in storage over extended periods of time without appreciable deterioration as measured by gum formation and/or the formation sediment. Thermal stability is also defined as the

ability of the liquid to withstand relatively high temperatures for short periods of time without the formation of sediment (i.e., carbonaceous deposits and/or coke). Thermal oxidative stability is the ability of the liquid to withstand relatively high temperatures for short periods of time in the presence of oxidation and without the formation of sediment or deterioration of properties (ASTM D2416), and there is standard equipment for various oxidation tests (ASTM D4171). Stability is also as the ability of the liquid to withstand long periods at temperatures up to 100°C (212°F) without degradation. Determination of the reaction threshold temperature for various liquid and solid materials might be beneficial (ASTM D2887).

Typically, gum is formed by any of the above-named reaction types during storage; some classes of hydrocarbons in fuel blends, particularly olefin derivatives and diolefin derivatives, are able to slowly react, at ambient temperatures, with the oxygen in the air. The oxidation products are responsible for the formation of an insoluble solid, commonly called deposits or gums, which sticks to the metal surfaces along the vehicle-fuel system, from the tank to the combustion chamber. Accumulation of these products can cause engine wear and can have adverse effects on engine efficiency, performance, emission, and durability. Consequently, it is necessary to predict fuel blend behavior and prevent gum formation, improving gasoline quality and using additives.

Hadley Cell

The Hadley cell is an air circulation pattern that dominates the tropical atmosphere, with rising motion near the equator, poleward flow 6 to 10 miles kilometers above the surface, descending motion in the subtropics, and flow near the surface toward the equator. This circulation is intimately related to the trade winds, tropical rain belts, subtropical deserts, and the jet streams.

The major driving force of atmospheric circulation is solar heating, which on average is largest near the equator and smallest at the poles. The atmospheric circulation transports energy in the direction of the poles, thereby reducing the resulting equator-to-pole temperature gradient. The mechanisms by which this is accomplished differ in tropical and extratropical latitudes. Between 30°N and 30°S latitude, this energy transport is accomplished by a relatively simple overturning circulation, with rising motion near the equator, poleward motion near the tropopause, sinking motion in the subtropics, and an equatorward return flow near the surface. In higher latitudes, the energy transport is instead accomplished by cyclones and anticyclones that cause relatively warm air to move toward the pole and cold air to move toward the equator in the same horizontal plane. The tropical overturning cell is referred to as the Hadley cell. Questions as to why it extends only to 30 degrees latitude and what determines its strength are at the heart of modern dynamical meteorology. The Hadley cell carries heat and moisture from the tropics to the northern and southern mid-latitudes. Near the tropopause, as the air moves toward the poles in the Hadley cell, it is turned eastward by the Coriolis force, which turns winds to the right in the Northern hemisphere and to the left in the Southern Hemisphere, creating the subtropical jet streams that flow from west to east.

As the ring of air moves toward the pole, it contracts closer to the axis of rotation so it must spin faster, which creates jets that rotate more rapidly than the Earth itself, which therefore appear as jets flowing from west to east with respect to the surface. Analogously, near the surface, the equatorward return flow is rotated to the west, or is slowed from the perspective of a non-rotating observer due to its movement away from the axis of rotation. These surface winds, with both an equatorward and a westward component, are referred to as the trade winds.

The region in which the equatorward moving surface flows converge and rise is known as the intertropical convergence zone (ITCZ) which is a high-precipitation band of thunderstorms. Having lost most of its water vapor to condensation and rain in the upward branch of the circulation, the descending air is dry. Low relative humidity is produced as the air is adiabatically warmed due to compression as it descends into a region of higher pressure. The subtropics are relatively free of the convection, or thunderstorms, that are common in the equatorial belt of rising motion. Many of the deserts of the world are located in these subtropical latitudes.

See also: Atmosphere, Coriolis Force, Ferrel Cell, Polar Cell, Walker Circulation, Wind Energy, Wind Power.

Halite

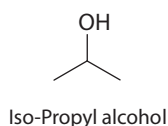
Halite (sometimes referred to as rock salt) is the natural mineral form of sodium chloride (NaCl), commonly known as and exists as isometric crystals. The mineral is typically colorless to yellow, but may also be light blue, dark blue, and pink depending on the amount and type of impurities. Halite commonly occurs with other evaporite deposit minerals such as several of the sulfates, halides, and borates.

Halite occurs in beds of sedimentary evaporite minerals that result from the drying up of enclosed lakes, playas, and seas. Halite is mainly a sedimentary mineral that usually forms in arid climates where ocean water evaporates. However, many inland lakes such as the Great Salt Lake of North America and the Dead Sea between Jordan and Israel are also locations where halite is forming. Over geologic time, several enormous salt deposits have been formed when repeated episodes of seawater evaporation occurred in restricted basins. Some of these deposits are thousands of feet thick. When buried deeply, they can erupt to form salt domes which are vertical diapirs (a domed rock

formations in which a core of rock has moved upward to pierce the overlying strata). Salt domes contain anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and native sulfur, in addition to halite and the potassium mineral sylvite (KCl).

Halite is highly soluble, so dissolve in the presence of undersaturated water and when the halite dissolves, non-halite lithologies in the layered evaporite sequence remain as a layer of caprock at the top of the diapir. On continental margins, caprock is common onshore, may develop during major sea-level low-stands on the shelf, and is largely absent in deepwater settings. If the salt is exposed at the sea floor, dissolution occurs, but salt diapirs in deepwater are almost always covered by a thin veneer of hemipelagic mud that protects the halite from dissolution.

Halite forms an important cement in certain formations – especially those with a high formation water salt concentration. The challenge in cleaning samples containing halite is to remove salt from the pore water and yet not dissolve the natural halite cement. The selected cleaning method must remove the formation water and its salts without significantly affecting the native halite cement content. Methanol will dissolve both, so it is recommended to use iso-propyl alcohol (propan-2-ol, $\text{CH}_3\text{CHOHCH}_3$) as the solvent.



It is difficult (if not impossible) to avoid some dissolution of the native halite, but the relatively large surface area of the precipitated salts will cause them to be dissolved more rapidly than cementing halite, which has a relatively small exposure surface. As direct application of water-miscible solvents (such as methanol and iso-propyl alcohol) with saline pore brine can often cause precipitation, the initial stage of cleaning should therefore attempt to remove a significant volume of water prior to application of the iso-propyl alcohol.

Hardwood

In the current context of using wood as an alternate energy source, a description of the different types of pore system is worthy of note since the type of wood and the distribution patterns of the pore systems can have a strong influence the processibility of the wood.

Wood (also known as xylem) serves two functions in a standing tree. One function is to keep the tree standing tall and to withstand wind. The second function is to move water and nutrients from the soil to the leaves of the tree. After a tree has been harvested, water will continue to move in and out of the wood freely. There are three surfaces, or planes, that can be used to identify wood.

When a tree is cut down, the flat surface of the stump is the cross-sectional surface. The cross-sectional surface shows most of the cell types needed to identify wood. The tangential surface is the next most important surface, followed by the radial surface. There are several wood types within a tree. They are named based on when the wood was formed or where the wood is within the tree. Heartwood is the center of older trees and is often darker because of the chemicals deposited there as the tree ages. Sapwood is the younger wood in a tree and is active in transporting water and nutrients. It generally has a lighter color and is closer to the bark. Each year, trees add one growth ring. Each growth ring is usually two different colors. A lighter portion, called earlywood, is formed in the spring. Latewood is darker and formed in the summer. Figure 2 shows the difference in earlywood and latewood in a piece of Southern yellow pine

Thus, trees are classified into two different types: (i) hardwoods and (ii) softwoods. This classification has nothing to do with the wood itself, but with the type of leaves and flowers the tree has. Approximately 90 to 95% of softwood cells are called longitudinal tracheids because they transport water, and there are so few cell types in softwoods making it difficult to distinguish between types of softwoods. The structure of hardwoods is much more complex, and there is considerable variation from one species of tree to another in hardwoods. Hardwoods contain vessel elements, or pores, that softwoods do not have. Pores vary greatly; they can be (i) small, (ii) large, (iii) present in great numbers, or (iv) almost completely absent. If pores are present, the wood is a hardwood. If no pores are present, it is likely a softwood.

In addition, hardwoods can be classified into three groups based on the pores: (i) ring-porous hardwoods such as oaks and elms which have pores that transition from small to large abruptly from the earlywood to the latewood, (ii) semi-ring porous hardwoods, such as walnut, pecan, and hickory have pores that gradually change from small to large in a growth ring, and (iii) diffuse-porous hardwoods, such as yellow poplar, gum, and maple which have pores that are the same size throughout the growth ring. In addition, the pores are also distributed in other ways in wood and can be arranged as (i) solitary pores, which are individual pores that are evenly spaced, (ii) pore chains, which are multiple pores that are chained together, (iii) nested pores, which are clusters of pores that are connected together, (iv) multiple pore system in which two or more pores are clustered together, and (v) wavy bands, which are bands of pores with a wavy appearance.

See also: Wood, Wood – Hardwood, Wood - Softwood.

Hazardous Air Pollutant

A hazardous air pollutant (HAP) is an air pollutant which presents, through inhalation or other routes of exposure, a threat of adverse human health effects or adverse environmental effects whether through ambient concentrations, bio-accumulation, deposition, or otherwise. Thus, hazardous air pollutants (HAPs) are air contaminants, frequently referred to as “air toxics,” that are known or suspected to cause serious human health effects or adverse environmental effects. Examples of hazardous air pollutants include benzene, trichloroethylene, mercury, chromium, and dioxin. The criteria air pollutants such as ozone and particulate matter are excluded from the hazardous air pollutants list.

Most air toxics originate from human-made sources, including mobile sources (such as automobiles, trucks, buses) and stationary sources (such as factories, refineries, power plants), as well as indoor sources (such as building materials and cleaning). There are two types of stationary sources that generate routine emissions of air toxics: (i) major sources and (ii) area sources.

Major sources typically are large industrial facilities such as chemical manufacturing plants, refineries, and waste incinerators. These sources may release air toxics from equipment leaks, when materials are transferred from one location to another, or during discharge through emission stacks or vents. Thus, major sources are defined as sources that emit 10 tons per year of any of the listed toxic air pollutants, or 25 tons per year of a mixture of air toxics. These sources may release air toxics from equipment leaks, when materials are transferred from one location to another, or during discharge through emission stacks or vents.

Area sources typically are smaller stationary facilities such as dry cleaners, auto body repair shops, and small manufacturing operations. These pollutants are typically emitted into the environment over the course of a year through normal emissions, fugitive releases, accidental releases, or plant upsets. The combination of volatile hydrocarbon derivatives and oxides of nitrogen also contribute to ozone formation, one of the most important air pollution problems. Thus area sources consist of smaller-size facilities that release lesser quantities of toxic pollutants into the air. Area sources are defined as sources that emit less than 10 tons per year of a single air toxic, or less than 25 tons per year of a combination of air toxics. Though emissions from individual area sources are often relatively small, collectively their emissions can be of concern - particularly where large numbers of sources are located in heavily populated areas. Though emissions from individual area sources often are relatively small, collectively they can be of concern, particularly where large numbers of sources are located in heavily populated areas.

Mobile sources include both on-road sources, such as cars, light trucks, large trucks, and buses, and non-road sources such as farm and construction equipment, lawn and garden equipment, marine engines, aircraft, and locomotives. Some hazardous air pollutants are also emitted from natural sources such as volcanoes.

Health effects associated with hazardous air pollutants include cancer, asthma and other respiratory ailments, birth defects, reproductive effects, and neurodevelopmental effects. However, although many hazardous air pollutants are of concern due to their potential to cause cancer, a substantial number of hazardous air pollutants lack evidence of cancer either because the relevant long-term studies have not been conducted, or because studies have been conducted and do not indicate carcinogenic potential.

See also: Hazardous Chemicals.

Hazardous Chemicals

A hazardous chemical is any chemical which can cause a physical or a health hazard. Chemical hazards arise from the inherent (i) flammable, (ii) explosive, (iii) toxic, (iv) carcinogenic, (v) corrosive, (vi) radioactive, or (vi) reactive properties. The effect of exposure on personnel may be acute, e.g., in a flash-fire or due to inhalation of a high concentration of an irritant vapor. Alternatively, prolonged or intermittent exposure may result in an occupational disease or systemic poisoning. Generally, acute effects are readily attributable; chronic effects, especially if they follow a long latency period or involve some type of allergic reaction to a chemical, may be less easy to assign to particular occupational exposures. Chemicals displaying any of the above properties can lead to several effects and a combination of hazards. For example, personnel exposed to a fire may be subject to flames, radiant heat, spilled liquid chemicals and vapours from them, leaking gases, and the pyrolytic and combustion products generated from chemical mixtures together with oxygen deficient atmospheres.

However, whether a hazardous condition develops in any particular situation also depends upon the physical properties of the chemical (or mixture of chemicals), the scale involved, the circumstances of handling or use, e.g., the processes involved and degree of containment, and upon the control measures prevailing, e.g., provision of control and safety devices, local exhaust ventilation, general ventilation, personal protection, atmospheric monitoring, and systems of work generally.

The issues to be held in consideration are (i) the nature of the toxicity presented by the constituent, (ii) the concentration of the constituent in the waste, (iii) the potential of the constituent or any toxic degradation product of the constituent to migrate from the waste into the environment under the types of improper management, (iv) the persistence of the constituent or any toxic degradation product of the constituent, (v) the potential for the constituent or any toxic degradation product of the constituent to degrade into non-harmful constituents and the rate of degradation, (vi) the degree to which the constituent or any degradation product of the constituent accumulates in an ecosystem, (vii) the plausible types of improper management to which the waste could be subjected, (viii) the quantities of the waste generated at individual generation sites or on a regional or national basis, (ix) the nature and severity of the public health threat and environmental damage that has occurred as a result of the improper management of wastes containing the constituent, and (x) actions taken by other governmental agencies or regulatory programs based on the health or environmental hazard posed by the waste or waste constituent. Such lists of chemicals are not always complete, and omission of a chemical from this list does not mean it is without toxic properties or any other hazard. In fact, hazard recognition and assessment always commence from a knowledge of the individual properties of a chemical that are relevant to behavior on spillage or emission, and determination of permissible levels for disposal to air, land, or water systems. Other properties may be relevant, such as odor which can serve as a means of detection.

See also: Hazardous Air Pollutants.

Hazardous Waste

A hazardous waste is a waste with properties that make it dangerous or capable of having a harmful effect on human health or the environment. Hazardous waste is generated from many sources ranging from industrial manufacturing process wastes to batteries – even during the development of alternative energy sources – and may come in many forms, including gases, liquids, solids, and sludge.

Thus, a waste is a hazardous waste if it is specifically listed as a known hazardous waste or meets the characteristics of a hazardous waste. Listed wastes are wastes from common manufacturing and industrial processes and specific industries, and can be generated from discarded commercial products. Characteristic wastes are wastes that exhibit any one or more of the following characteristic properties: ignitability, corrosivity, reactivity, or toxicity.

The types of hazardous wastes classified by the United States Environmental Protection Agency in Subpart C of 40 CFR 61 consist of solid, liquid, and gaseous streams. They can be further classified as: (i) inorganic or organic, (ii) metal or non-metal, (iii) aqueous or non-aqueous, (iv) halogenated or non-halogenated, (v) ignitable or non-ignitable, (vi) corrosive or non-corrosive, (vii) reactive or non-reactive, and (viii) toxic or non-toxic.

However, many hazardous materials can display more than one of the above properties, and their waste streams become more complex through mixing a contamination as they pass down the waste hierarchy and get farther from the place at which they were generated. It is much simpler to recover materials for reuse when they have not been cross-contaminated with other hazardous wastes or for that matter any other wastes. Therefore, it is usually desirable to set use, recovery, and recycling equipment as near the waste generation site as possible and in any case to segregate waste streams to prevent cross-contamination.

Some waste streams are not compatible and should not be mixed unless special safety precautions have been taken to protect against the hazards generated by the mixing. An example of such incompatible waste streams is provided by an aqueous acid stream and a second stream containing either soluble sulfides or cyanides. Mixing would generate extremely toxic HCN or hydrogen sulfide gases. Such incompatible waste streams usually involve corrosive or reactive wastes as one of the waste streams.

In many cases, the feedstocks to separation processes were classified as (i) heterogeneous or (ii) homogeneous. Typically, heterogeneous streams are usually relatively easy to separate into their respective phases. When phase separation alone provides the necessary recovery process, as is often the case with oily wastewaters, recovery of valuable materials can be achieved by the use of coalescing and settling devices. However, homogeneous waste streams require more complex processes such as distillation, extraction, or adsorption for recovery of valuable materials.

See also: Hazardous Chemicals, Waste.

H-Coal Process

The H-coal process is an extension of the ebullated-bed technology that is used to convert coal, heavy crude oil, and residua into lower boiling liquid products. The process also has the potential to be adaptable for the conversion of certain types of biomass and/or waste to low-boiling liquid products. There is also the potential for the process to be adapted to the conversion of biomass and/or waste to renewable fuels.

In the process, the feedstock is crushed, slurried with oil (usually recycle oil from the process) and pumped to a pressure of up to 3,000 psi after which the mixture is preheated and introduced into the bottom of the ebullated-bed reactor. The overhead products are fractionated into gases, low-boiling distillate, and high boiling-distillate. The process conditions (which may be 345 to 370°C; 650 to 700°F) can be altered appropriately to accommodate different feedstocks and to produce different product slates. For example, synthetic crude production usually requires higher temperatures and higher hydrogen (partial) pressures than the process conditions for the production of low-sulfur residual oils in addition; this latter operational mode requires that less hydrogen be consumed.

See also: Biomass, waste.

Heat Balance

Every chemical process involves the transfer of energy, typically in the form of heat. For example, the distillation process involves phase changes in which energy is added for volatilization at reboiler and energy removed at condenser which the amount of energy that flows into or out of each process unit, that must be added or removed. Heat balance calculations are usually carried out when developing new chemical processes and improving old ones, because no process can work if too much heat is released or if there is a lack of thermal energy to maintain the reaction temperature.

The heat balance of, for example, the combustion process provides a relative weighting of the heat input into the system versus the heat output of the process:

$$dH_I \rightarrow dH_c + S_H + dH_E$$

In this equation, dH_c is the heat input, S_H is a composite of the sensible and latent heats of air, fuel, and other materials, and dH_E is the heat from exothermic reactions (other than combustion) which may contribute to the overall combustion process:

$$dH_o \rightarrow dH_{cu} + S_{HC} + dH_{-E} + dS_{AG} + dH_L$$

dH_o is the heat output, dH_{cu} is the heat of combustion of unburned fuel, S_{HC} is the sensible and latent heats in the carbonization products, dH_{-E} is the heat absorbed by endothermic reactions, dS_{AG} is the sensible and latent heats in the combustion products (ash and stack gases), and dH_L is the heat losses to the surroundings by convection, radiation, and combustion.

The presence of water vapor in the combustion system appears in the latent heat effects, and one consequence of high moisture content in coal combustion is that a part of the heat is lost due to evaporation of the moisture in the coal and is not recouped from the combustion products.

A small amount (<5% w/w) of water in the feedstock (such as biomass) may not exert any marked effect on the overall heat requirements, since the sensible heat of the gases vaporizes the water.

Heat Capacity

The heat capacity of the feedstock is the heat required to raise the temperature of one unit weight of the feedstock by one degree.

The heat capacity can be measured by standard calorimetric methods that have been developed for other materials (ASTM C351). The units for heat capacity are Btu per pound per degree Fahrenheit (Btu/lb/°F) or calories per gram per degree centigrade (cal/g °C), but the specific heat is the ratio of two heat capacities and is therefore dimensionless.

The heat capacity of water is 1.0 Btu/lb °F and the heat capacity of any material will always be numerically equal to the specific heat. Consequently, there has been the tendency to use the terms heat capacity and specific heat almost equivocally.

The specific heat usually increases with its moisture content, decreases with carbon content, and increases with volatile matter content, with mineral matter content exerting a somewhat lesser influence. The values for the specific heat of various coals fall into the general range 0.25 to 0.37 but, as with other physical data, comparisons should only be made on an equal basis (e.g., moisture content, mineral matter content, etc.).

Estimates of the specific heat have also been made on the assumption that the molecular heat of a solid material is equal to the sum of the atomic heats of the constituents (Kopp's law); the atomic heat so derived is divided by the atomic weight to give the (approximate) specific heat. Thus, using coal as the example, it has been possible to derive a formula that indicates the relationship between the specific heat and the elemental analysis of coal (mineral-moisture-free basis, mmf basis):

$$C_p = 0.189C + 0.874H + 0.491N + 0.360O + 0.215S$$

C, H, N, O, and S are the respective amounts (% w/w) of the elements in the coal.

See also: Kopp's Law.

Heat Content

The heat content or calorific value of a material is a direct indication of the heat content (energy value) of the material and a means by which coal can be evaluated.

The heat content of a feedstock (usually presented in Btu/lb) is a direct indication of the energy value of the feedstock and represents the combined heat of combustion of the carbon, hydrogen, nitrogen, and sulfur in the organic.

In the present context, the importance of the calorific value is one of the means by which biomass and fuels can be evaluated (for example, Table H-1).

Table H-1 Heat content (calorific value, btu/lb) of selected hydrocarbons and fuels.

Fuel	Heat content, Btu/lb
Acetylene	20,734
Bagasse (sugar cane)	6,500
Biomass (corn stover, dry)	7,000
Biomass (forest residue, dry)	6,600
Biomass (herbaceous, dry)	7,400
Butane	19,679
Carbon monoxide	4,346
Ethane	20,431
Ethylene	20,276
Hydrogen	51,593
Methane	21,518
Natural gas*	21,150
Producer gas	2,280
Rice Hulls	6,580
Poultry litter	6,180
Propane	19,944
Switchgrass	7,300
Wood (farmed trees, dry)	8,400
Wood (forest residue, dry)	8,400
Crude oil*	18,000
Heavy oil*	16,000
Coal (anthracite)*	14,000
Coal (bituminous)*	11,000
Coal (lignite)*	8,000

*Included for comparison.

The calorific value is a complex function of the elemental composition and is usually reported as the gross calorific value with a correction applied if the net calorific value is of interest.

Depending on the material, it is possible to make a close estimation of the calorific value (CV) by means of various formulae (that have been developed for coal and might require some modification), the most popular of which are:

The Dulong formula:

$$CV = 144.4(\%C) + 610.2(\%H) - 65.9(\%O) - 0.39(\%O)$$

The Dulong-Berthelot formula:

$$CV + 81370 + 345 [\%H - (\%O + \%N - 1)/8] + 22.2(\%S)$$

%C, %H, %N, %O, and %S are the respective carbon, hydrogen, nitrogen, oxygen, and organic sulfur contents of the material (all of which are calculated to a dry, ash-free basis).

In terms of energy content and energy density, There are two kinds of heat of combustion: (i) the higher value (HHV), or gross heat of combustion, includes all the heat released as the products cool to room temperature and whatever water vapor is present condenses, and (ii) the lower value (LHV), or net heat of combustion, does not include the heat which could be released by condensing water vapor, and may not include the heat released on cooling all the way down to room temperature.

See also: Energy Density, Higher Heating Value, Lower Heating Value.

Heat Exchangers

Heat exchangers transfer heat from one working fluid to another. For instance, steam generators, feedwater heaters, reheaters and condensers are all examples of heat exchangers found in nuclear power systems. The heat transfer rate across a heat exchanger is usually expressed in the form:

$$Q = UA\Delta T_m$$

Q is the heat transfer rate, U is the overall heat transfer coefficient, A is the heat exchanger area, and ΔT_m is the average temperature difference between the fluids Table H-2).

Table H-2 Various types of gas-liquid heat exchangers.

Driving force	Change of phase	Examples
Gravity	No	Spray columns, packed columns
	Yes	Cooling towers, falling droplet evaporators
Forced	No	Spray coolers/quenchers
Liquid flow	Yes	Spray condensers/evaporation
Gravity	No	Bubble columns, perforated tray columns
	Yes	Bubble column condensers
Forced	No	Gas spargers
Gas flow	Yes	Direct contact evaporators

However, heat exchangers exist in three primary forms: (i) parallel flow heat exchangers, (ii) counter-flow heat exchangers, and (iii) cross-flow heat exchangers. classifications of heat exchangers according to their flow arrangement.

In *parallel-flow* heat exchangers, the two fluids enter the exchanger at the same end, and travel in parallel to one another to the other side. In *counter-flow* heat exchangers, the fluids enter the exchanger from opposite ends. The countercurrent design is the most efficient, in that it can transfer the most heat from the heat (transfer) medium per unit mass due to the fact that the average temperature difference along any unit length is *higher*. In a *cross-flow* heat exchanger, the fluids travel roughly perpendicular to one another through the exchanger.

Heat exchangers are designed to maximize the surface area of the wall between the two fluids, while minimizing resistance to fluid flow through the exchanger. The exchanger's performance can also be affected by the addition of fins or corrugations in one or both directions, which increase surface area and may channel fluid flow or induce turbulence.

Direct contact heat exchangers involve heat transfer between hot and cold streams of two phases in the absence of a separating wall. Thus such heat exchangers can be classified as: (i) gas-liquid, (ii) immiscible liquid-liquid, and (iii) solid-liquid or solid-gas. Most direct contact heat exchangers fall under the gas-liquid category, where heat is transferred between a gas and liquid in the form of drops, films or sprays. In the petroleum and natural gas industry, these types of heat exchangers are used predominantly in liquid heating, water cooling and, condensing.

For an adiabatic heat exchanger (no heat transferred with environment), there are three equations for Q , i.e., the rate of heat exchange between the two process streams:

$$Q = N_{ps} (H_{ps,in} - H_{ps,out}) \text{ (heat transferred from process stream)}$$

$$Q = N_{us} (H_{us,out} - H_{us,in}) \text{ (heat transferred to utility stream)}$$

$$Q = UAF\Delta T_{avg} \text{ (rate of heat transfer; actually defining } U)$$

Q is the rate of heat exchange (e.g., in kJ/h), N_i is the flowrate of stream i (e.g., in kmol/h), H_i is the specific enthalpy of stream i (kJ/kmol), U is the overall heat transfer coefficient (kJ/m²K), A is the heat exchange area (m²), F is the correction factor for the deviation from cocurrent or countercurrent flow, ΔT_{avg} is the average temperature difference between the streams for true cocurrent or countercurrent flow.

If both streams exchange either latent heat or sensible heat, but not both, then:

$$\Delta T_{avg} = \Delta T_{lm} \equiv \frac{\Delta T_{end1} - \Delta T_{end2}}{\ln \Delta T_{end1} - \ln \Delta T_{end2}}$$

for both cocurrent and countercurrent flow, where: ΔT_{end1} is the temperature difference between the two streams at end 1 of the column (K), ΔT_{end2} is the temperature difference between the two streams at the end 2 of the column (K). Either end of the heat exchanger can be designated as 1 or 2.

Heating Value

The heating value (heat content, calorific value, or energy value) of a substance, usually a fuel, is the amount of heat released during the combustion of a specified amount of it.

The lower heating value (usually represented as LHV, also known as net calorific value) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C, 77°F) and returning the temperature of the combustion products to 150°C (300°F), which assumes the latent heat of vaporization of water in the reaction products is not recovered.

The higher heating value (usually represented as HHV, also known gross calorific value or gross energy) of a fuel is defined as the amount of heat released by a specified quantity (initially at 25°C, 77°F) once it is combusted and the products have returned to a temperature of 25°C (77°F), which takes into account the latent heat of vaporization of water in the combustion products.

See also: Calorific Value, Heat Content.

Heat of Combustion

The gross heat of combustion is given with fair accuracy by the equation:

$$Q = 12,400 - 2100d^2$$

Where d is the 60/60°F specific gravity. Deviation is generally less than 1%, although many highly aromatic feedstocks may show considerably higher values.

For thermodynamic calculation of equilibria useful in hydrocarbon research, combustion data of extreme accuracy are required because the heats of formation of water and carbon dioxide are large in comparison with those in the hydrocarbon derivatives. Great accuracy is also required of the specific heat data for the calculation of free energy or entropy. Much care must be exercised in selecting values from the literature for these purposes, since many of those available were determined before the development of modern calorimetric techniques.

See also: Heat Balance.

Heavy Metals

Heavy metals are those metals that have relatively high density, atomic weight, or atomic number. As an example, a density that is higher than 5 g/cm³ is often used as a guide to the definition of the heavy metals. However, the physical and chemical characterization of heavy metals need to be treated with caution, as the metals involved are not always consistently defined. While it is relatively easy to distinguish a heavy metal such as tungsten from a lower atomic weight metal such as sodium, a few heavy metals, such as zinc, mercury, and lead, have some of the characteristics of lower atomic weight metals, and lower atomic weight metals such as beryllium, scandium, and titanium have some of the characteristics of the higher atomic weight metals.

Heavy metals are natural elements characterized by their rather high atomic mass and their high density. Although typically occurring in rather low concentration, they can be found all through the crust of the Earth. Commonly, a density of at least 5 g cm⁻³ is used to define a heavy metal and to differentiate it from other, lower atomic weight metals. Other, broader definitions for "heavy metals" require an atomic mass higher than 23 or an atomic number exceeding 20; these definitions are highly error-prone and confusing.

Examination of the periodic table of elements (Table H-3) shows that (according to the density criterion) heavy metals occupy columns 3 to 16, of the periods 4 to 6, encompassing the transition metals, post-transition metals, and lanthanides.

Table H-3 The Periodic Table of the Elements.

1																	18
1 H 1.01	2 He 4.00																
3 Li 6.34	4 Be 9.01											5 B 10.31	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 51.99	25 Mn 54.94	26 Fe 55.85	27 Co 56.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (208.98)	85 At 209.99	86 Rn 222.02
87 Fr 223.03	88 Ra 226.03	89-103	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (278)	110 Ds (281)	111 Rg (282)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 144.91	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.06	71 Lu 174.97			
89 Ac 227.03	90 Th 229.04	91 Pa 231.04	92 U 235.03	93 Np 237.05	94 Pu 244.06	95 Am 243.06	96 Cm 247.07	97 Bk 247.07	98 Cf 251.08	99 Es (254)	100 Fm 257.10	101 Md 258.1	102 No 259.10	103 Lr (262)			

Some heavy metals – such as copper, selenium, or zinc – are essential trace elements, with functions indispensable for various biological processes also driving the entire human metabolism. The heavy metal cobalt, acting as the central atom in the vitamin B12 complex, is a key player in the reductive branch of the propionic acid fermentation pathway.

Many heavy metals such as iron, zinc, tin, lead, copper, and tungsten are of outstanding technological significance insofar as the metal acts as the central atom of bioinorganic catalysts for special chemical transformations. However, many of the heavy metals such as mercury, cadmium, arsenic, chromium, thallium, lead, and others exert toxic effects, even at low concentration.

There are some trace elements among the heavy metal family, which are essential for many biological processes; they are predominantly found in Period 4 of the Periodic Table of Elements. For strict aerobic beings as humans are, it would not be possible to survive without having cytochromes, which make aerobic life forms breathe since the very beginning. Iron also plays a major role in the human respiration system as the central atom of the blood pigment heme. Copper plays a similar role in the transport of electrons and oxygen, especially as the central atom in hemocyanin in mollusks and arthropods. Zinc in turn is pivotal as a constituent of some enzymes. Selenium is described as an antioxidant; further, it is involved in hormone biosynthesis. Cobalt was found to be significant in the biosynthesis of complex compounds and different steps in cellular metabolism, especially as the central atom in vitamin B12, which is needed for cell division, blood formation, the nervous system, and in propionic acid biosynthesis. Moreover, vanadium and manganese are important for regulation and functioning of several enzymes, whereas some metabolic functions are also assigned to the typically known-as-toxic elements chromium, arsenic, and nickel. Regarding arsenic, this element was only recently revealed as a natural constituent in herring caviar, where it was shown to substitute phosphorus in phosphatidylcholine-like lipids, the so-called arseno-lipids. Further, molybdenum plays a role in some redox reactions, in addition to the function of cadmium in the metabolism of some microalgae from the Diatomophyceae class.

Significantly elevated levels of inorganic pollutants, of which the so-called heavy metals are prominent, often occur in soils from previously heavily industrialized areas. These sites produced wastes contaminated with heavy metals, arsenic, and antimony. Following the decline of heavy manufacturing, many industrial sites have been abandoned and remain so without remedial works to their contaminated and often phytotoxic substrates.

Toxic metals, such as lead (Pb), are problematic contaminants in soils, surface waters, recent sediments, and aerosols, mainly in urban environments. Toxic metals occur naturally in mining areas, but the mining activities reinforce their release into the environment. Because of their limited mobility, toxic metals are less frequent in groundwater and often form cations (such as divalent lead, Pb^{2+}) that are prone to adsorption, or they precipitate as difficult-to-dissolve oxide derivatives, sulfide derivatives, or other minerals. Some metal cations are more mobile in the environment such as cadmium (Cd^{2+}), which is also highly toxic. Mercury is extremely toxic and specific bacteria can convert it into the highly mobile methyl mercury ion (HgCH_3^+) or volatile dimethyl mercury [$\text{Hg}(\text{CH}_3)_2$]. In karst systems, sediments in conduits and caves can act as reservoirs for toxic metals and other contaminants; during high-flow events, they can be mobilized and conducted toward large springs.

Arsenic (As) is a toxic metal that causes large-scale groundwater contamination and diseases in several regions of the world. Natural arsenic contamination occurs in arid to semiarid inland basins and in reducing alluvial aquifers, that is, in flat, low-lying areas, where groundwater is sluggish and often exploited by deep pumping wells. Arsenic-rich water is also found in mining areas; in the past, it was also used for insecticides, some of which might still be in use in some regions.

Modern physical and chemical approaches for remediation of heavy metal pollution involve the use of adsorption on new adsorbents such as nano-carriers, ion exchange techniques, removal via advanced membrane filtration techniques, electrodialysis, or photocatalysis. Among these novel physicochemical techniques, new adsorption- and membrane filtration-based methods are most thoroughly investigated and are most commonly applied to treat contaminated wastewater. Among new absorbents, both inorganic (kaolinite, montmorillonite) and organic materials (such as agricultural waste or bio-char) were studied for heavy metal recovery. In this context, the application of carbon-based, metal-based, or metal oxide-based nanoparticles as adsorbents benefits from high surfaces susceptible toward metal adsorption and expedient reactivity. The mechanisms of interactions of nanomaterials with, on the one hand, heavy metals and, on the other hand, heavy metal with additional wastewater constituents with metal-binding groups need to be understood in order to optimize the recovery processes.

Heavy Oil

Heavy oil (heavy crude oil) is a type of crude oil that is different from conventional crude oil insofar as they are much more difficult to recover from the subsurface reservoir. Heavy crude oil, particularly heavy crude oil formed by biodegradation of organic deposits, is found in shallow reservoirs, formed by unconsolidated sands. This characteristic, which causes difficulties during well drilling and completion operations, may become a production advantage due to higher permeability. In simple terms, heavy crude oil is a type of crude oil which is very viscous and does not flow easily. The common characteristic properties (relative to conventional crude oil) are high specific gravity, low hydrogen-to-carbon ratios, high carbon residues, and high contents of asphaltenes, heavy metal, sulfur, and nitrogen. Specialized refining processes are required to produce more useful fractions, such as: naphtha, kerosene, and gas oil.

Heavy crude oil has a much higher viscosity (and lower API gravity, typically on the order of $<20^\circ$ API) than conventional crude oil, and recovery of heavy crude oil usually requires thermal stimulation of the reservoir. When crude oil occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark-to-light-colored liquid, it is often referred to as conventional crude oil.

The term heavy crude oil has also been arbitrarily (incorrectly) used to describe both the heavy crude oils that require thermal stimulation of recovery from the reservoir and the bitumen in bituminous sand (tar sand) formations from which the viscous bituminous material is recovered by a mining operation. Extra heavy crude oil is a non-descript term (related to viscosity) of little scientific meaning, which is usually applied to tar sand bitumen and, like tar sand bitumen, is generally incapable of free flow under typical (low temperature) reservoir conditions.

Heavy Water Reactor

The heavy water reactor (HWR) differs in the design of the core, fuel, moderator, and coolant and the orientation of the core of the reactor which is horizontal inside a tank that consists of fuel channels. The reactor can be refueled during operation, using the natural uranium as fuel, and utilizing the heavy water as a coolant and moderator. Same as for pressurized water reactors, the heat is exchanged between the primary and secondary loop through a heat exchanger.

A pressurized heavy-water reactor (PHWR) is a nuclear reactor that uses heavy water (deuterium oxide, D_2O) as the coolant and neutron moderator. This types of reactor frequently use natural uranium as fuel, but can also use a low-enriched uranium. The heavy water coolant is kept under pressure to avoid boiling, allowing it to reach higher temperature (mostly) without forming steam bubbles, exactly as for the pressurized water reactor. The low absorptivity of the heavy water for neutrons greatly increases the neutron economy of the reactor, thereby avoiding the need for enriched fuel.

See: Nuclear Reactor – Heavy Water Reactor.

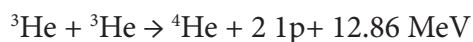
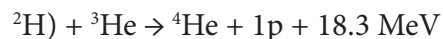
Helium-3

Helium-3 (3He) is a non-radioactive isotope of helium with two protons and one neutron. It is rare on Earth, and it is sought for use in nuclear fusion research. The nucleus of a helium-3 atom, consists of two protons but only one neutron, in contrast with two neutrons in common helium.

Because of the lower atomic mass (3.02 atomic mass units), helium-3 has some physical properties different from those of helium-4 (4.00 atomic mass units). Because of the weak, induced dipole–dipole interaction between helium atoms, their macroscopic physical properties are mainly determined by their zero-point energy (ground-state kinetic energy). Also, the microscopic properties of helium-3 cause it to have a higher zero-point energy than helium-4. This implies that helium-3 can overcome dipole–dipole interactions with less thermal energy than helium-4 can.

Helium-3 boils at $270^\circ C$ ($456^\circ F$) compared with helium-4 at $267^\circ C$ ($452^\circ F$) and the critical point is also lower at $270^\circ C$ ($454^\circ F$), compared with helium-4 at $268^\circ C$ ($450^\circ F$). Helium-3 has less than one-half of the density when it is at its boiling point: 59 gram per liter compared to the 125 gram per liter of helium-4 at a pressure of one atmosphere.

Helium-3 (^3H) can be used in fusion reactions by either of the reactions such as the reaction with deuterium (^2H) or with itself:



The conventional deuterium + tritium (D-T, ^2H - ^3H) fusion process produces energetic neutrons which render reactor components radioactive with activation products. The appeal of helium-3 fusion stems from the aneutronic nature of its reaction products, and helium-3 is non-radioactive. The lone high-energy by-product, the proton, can be contained using electric and magnetic fields. The momentum energy of this proton (created in the fusion process) will interact with the containing electromagnetic field, resulting in direct net electricity generation.

Because of the higher Coulomb barrier, the temperatures required for $^2_1\text{H} + ^3_2\text{He}$ fusion are much higher than those of conventional D-T fusion. Moreover, since both reactants need to be mixed together to fuse, reactions between nuclei of the same reactant will occur, and the D-D reaction ($^2_1\text{H} + ^2_1\text{H}$) does produce a neutron. Reaction rates vary with temperature, but the deuterium-helium-He-3 reaction rate is lower than the D-D reaction rate. Therefore, fusion using D- ^3He fuel may produce a somewhat lower neutron flux than D-T fusion.

The second possibility, fusing ^3_2He with itself ($^3_2\text{He} + ^3_2\text{He}$), requires even higher temperatures (since now both reactants have a +2 charge), and thus is even more difficult than the D- ^3He reaction. However, it does offer a possible reaction that produces no neutrons; the protons it produces possess charges and can be contained using electric and magnetic fields, which in turn results in direct electricity generation.

The amounts of helium-3 needed as a replacement for conventional fuels are substantial by comparison to amounts currently available. The total amount of energy produced in the $^2\text{H}_1 + ^3_2\text{He}$ reaction is 18.4 MeV. If the total amount of energy could be converted to electrical power with 100% efficiency (a physical impossibility), it would correspond to approximately 30 minutes of output of a gigawatt electrical plant per mole of ^3He .

See also: Nuclear Fission, Nuclear Fusion.

Hemicellulose

Unlike cellulose, hemicellulose derivatives consist of different monosaccharide units. In addition, the polymer chains of hemicellulose derivatives have short branches and are amorphous. Because of the amorphous morphology, hemicellulose derivatives are partially soluble in water. Hemicellulose derivatives are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. The hemicellulose derivatives, which are present in deciduous woods chiefly as pentosan and in coniferous woods almost entirely as hexosan, undergo thermal decomposition very readily. Hemicellulose derivatives are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micelles and fiber.

The backbone of the chains of hemicellulose derivatives can be a homopolymer (generally consisting of a single sugar repeat unit) or a heteropolymer (a mixture of different sugars). Among the most important sugar of the hemicellulose derivatives component is xylose. In hardwood xylan, the backbone chain consists of xylose units which are linked by β -(1,4)-glycoside bonds and branched by α -(1,2)-glycoside bonds with 4-O-methyl glucuronic acid groups. In addition, O-acetyl groups sometimes replace the OH groups in position C_2 and C_3 . For softwood xylan, the acetyl groups are fewer in the backbone chain, but softwood xylan has additional branches consisting of arabinofuranose units linked by α -(1,3)-glycoside bonds to the backbone. Hemicellulose derivatives are largely soluble in alkali and, as such, are more easily hydrolyzed.

See also: Biomass, Cellulose, Wood.

Hemp

Hemp is an annual short day, C3 plant with a high cellulose and lignin content in its stems and a high fat and protein content in its seeds. The entire plant consisting of bast fibers, leaves, seeds, and processable remains can be used as a

solid fuel when compacted. The stalk contains a strong and durable fiber. The average height is 2.5 meters, but it can reach up to 4 meters height. For the energetic use, the whole hemp crop is harvested. Direct harvesting by a forage harvester was tested.

Hemp can be easily planted and cultivated, but its growing is prohibited in some EU countries as it can be used as a drug. The plants vegetative period is approximately 100 days, with the main growth period in June and July, followed by flowering in August. The yields are high (18 t/ha), but the high plant moisture content can create storage problems.

Two different harvesting technologies are available for the energy use of the whole hemp crop. The first is the whole-fiber-technology where, with a modified chopping technology, the hemp culm is cut into 50 to 60 cm lengths. The straw stays for four weeks on the field for drying before the bales are pressed. Another technology is wet harvesting. This technology includes the chopping of the crops followed by silaging. For combustion, it is necessary to press the hemp silage into bales to reduce the water content of the fuel.

See also: Biomass.

Herbaceous Biomass

The energy application of herbaceous biomass has a high potential because most of it represents residual material from agriculture (straw), which could be available at a relatively low cost.

The transformation of herbaceous raw material into a feedstock for gasification is simpler than that of woody raw material since herbaceous biomass only requires chaffing. Hence, unlike woody biomass, a distinction between raw material and feedstock is not made for herbaceous biomass. The main herbaceous species currently considered for energy application are miscanthus, reed canary grass, and switchgrass.

Miscanthus is an attractive option, since growing requires lower input of fertilizers and pesticides compared to agricultural crops, while yields can reach 15 tonnes per hectare per year under optimum conditions. Its main disadvantage is that it can be difficult to rehabilitate the land for other uses due to the deep root structure of miscanthus. Slightly lower maximum yields (up to 4 ton per acre per year) are earned from switchgrass. Canary grass gives even lower yields (less than 2 tons per acre per year) without the need for crop rotation for approximately 10 years, but it fits well the climate conditions of northern countries. Canary grass is however very invasive of wetlands and is not a suitable alternative to agricultural crops on high grades of arable land.

Compared to short-rotation forestry, herbaceous species have lower moisture content and under certain conditions can be slightly cheaper. However, herbaceous species show some disadvantages compared to woody biomass: lower bulk density, which increases transportation and handling costs; a larger content of undesirable compounds (potassium, chlorine, sulfur, ash), which reduces the yield of synthesis gas, may cause corrosion, agglomeration, intensive slagging and fouling, etc. For these reasons, herbaceous biomass usually is not directly gasified for BTL production, but it is processed into a semi-finished product – pyrolysis oil.

See also: Herbaceous Crops.

Herbaceous Crops

Growing dedicated herbaceous crops for energy purposes is a relatively novel practice, thus complete information related to the various aspects of their cultivation is still scarce. The main herbaceous species currently considered in Europe for energy application are miscanthus, red canary grass, and switchgrass. Miscanthus is an attractive option, since growing requires lower input of fertilizers and pesticides compared to agricultural crops, while yields can reach 6 tons per acre per year under optimum conditions. Its main disadvantage is that it can be difficult to rehabilitate the land for other uses due to the deep root structure of miscanthus. Slightly lower maximum yields (up to 10 tonnes per hectare per year) are earned from switchgrass. Red canary grass gives even lower yields per hectare per year (5 to 7 tons) without the need for crop rotation for approximately 10 years. Red canary grass is however very invasive of wetlands and is not a suitable alternative to agricultural crops on high grades of arable land.

Compared to short-rotation forestry, herbaceous species have lower moisture content and under certain conditions can be slightly cheaper. However, herbaceous species show some disadvantages compared to woody biomass: lower bulk density, which increases transportation and handling costs; a larger content of undesirable compounds (potassium, chlorine, sulfur, ash), which reduces the yield of synthesis gas, may cause corrosion, agglomeration, intensive slagging and fouling, etc. For these reasons, herbaceous biomass usually is not directly gasified for BTL production, but it is processed into a semi-finished product – pyrolysis oil.

See also: Biomass, Crops, Energy from Crops.

Heteroatom Compounds

The term heteroatom compounds is usually used more specifically to indicate that non-carbon atoms have replaced carbon in the backbone of the molecular structure of a hydrocarbon derivative. Typical heteroatoms are nitrogen, oxygen, and sulfur and, to a lesser extent phosphorous, chlorine as well as various metals that are bound within the organic structure.

When present in organic compounds, atoms other than carbon and hydrogen are called hetero-atoms. Sulfur, nitrogen, oxygen, and metals are minor constituents of crude oil, but their impact on processing costs can be major. When burned in vehicles or power plants, high-sulfur fuels lead to the production of sulfur oxides and, eventually, cause acid rain. For many refining processes, sulfur is a catalyst poison. Nitrogen and metals also are catalyst poisons. Therefore, refiners devote a considerable amount of time and money to remove hetero-atoms from intermediate streams and finished products.

Within the class of heteroatom compounds are a class of compounds known as heterocyclic compounds which are any of a major class of organic chemical compounds characterized by the fact that some or all of the atoms in these molecules are joined in rings containing at least one atom of an element other than carbon. In the general structure, heterocyclic compounds resemble cyclic organic compounds that incorporate only carbon atoms in the rings but the presence of the heteroatoms (nitrogen, oxygen, or sulfur) gives heterocyclic compounds physical and chemical properties that are often quite distinct from those of their all-carbon-ring analogs.

Heterogeneous Catalyst

Catalysts can be divided into two main types – homogeneous and heterogeneous. In a homogeneous reaction, the catalyst is in the same phase as the reactants. A heterogeneous catalyst is a catalyst that exists in a different phase to the reactants. Heterogeneous catalysts provide a surface on which the reaction may take place.

In heterogeneous catalysis, in order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb from the surface and diffuse away from the solid surface. Frequently, this transport of reactants and products from one phase to another plays a dominant role in limiting the reaction rate. If diffusion rates are not taken into account, the reaction rates for various reactions on the catalyst surface depend solely on the rate constants and reactant concentrations. Asymmetric heterogeneous catalysis can be used to synthesize enantiomerically pure compounds using chiral heterogeneous catalysts.

Heterogeneous catalysts are typically supported insofar as the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Sometimes, the support is merely a surface upon which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction.

There are two types of heterogeneous catalyst: zeolite and amorphous catalysts. The difference between them is that zeolite catalysts are more active in cracking than amorphous catalysts due to its higher acidity in both strength and number of acid sites. Zeolite-based catalysts are also highly selective toward industrial products. For a given conversion of feedstock, the amorphous catalysts require a substantially higher operating

temperature than the zeolite-containing catalysts. Another major advantage of the zeolite catalysts is their lower rate of deactivation.

Heterosphere

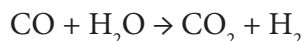
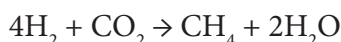
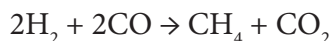
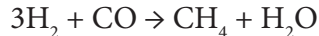
The heterosphere is the layer of an atmosphere where the gases are separated out by molecular diffusion with increasing altitude such that less dense constituents become more abundant relative to higher density constituents. The higher density constituents tend to be present in the lower layers of the heterosphere (density segregation or density stratification), while the lower density constituents are present at higher elevations. The exact boundaries between the different molecules vary according to temperature and solar activity. The heterosphere extends from the turbopause to the edge of the atmosphere and lies directly above the homosphere.

See also: Atmosphere.

High-Btu Gas

High-Btu gas consists predominantly of methane with a heating value of approximately 1,000 Btu/scf. It is also referred to as substitute (or synthetic) natural gas (SNG) depending on the origin of the gas. High-Btu gas consists mainly of pure methane (>95%), and as such, its heating value is around 900 to 1,000 Btu/scf.

This type of synthesis gas is usually produced by catalytic reaction of carbon monoxide and hydrogen, which is called methanation reaction. The feed synthesis gas usually contains carbon dioxide and methane in small amounts. Further, steam is usually present in the gas or added to the feed to alleviate carbon fouling that affects the catalytic effectiveness. Therefore, the pertinent chemical reactions in the methanation system include:



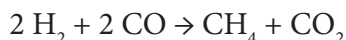
Among the above reactions, the most dominant chemical reaction leading to methane is the first one. Therefore, if methanation is carried out over a catalyst with a synthesis gas mixture of hydrogen and carbon monoxide, the desired hydrogen-to-carbon monoxide ratio of the feed synthesis gas is on the order of 3:1. The large amount of water produced is removed by condensation and recirculated as process water/steam. During this process, most of exothermic heat due to the methanation reaction is also recovered via a variety of energy integration processes. While all the reactions listed above are quite strongly exothermic except the forward water gas shift reaction being mildly exothermic, the heat release depends largely on the amount of carbon monoxide present in the feed synthesis gas. For each 1% of carbon monoxide in the feed synthesis gas, an adiabatic reaction will experience a 60°C (140°F) temperature rise, which may be termed as adiabatic temperature rise.

A variety of metals exhibit catalytic effects on methanation reaction. In the order of catalytic activity, $\text{Ru} > \text{Ni} > \text{Co} > \text{Fe} > \text{Mo}$. Nickel is by far the most commonly used catalyst in commercial processes because of its relatively low cost and also of reasonably high catalytic activity. Nearly all the commercially available catalysts used for this process are, however, very susceptible to sulfur poisoning, and efforts must be spent to remove all hydrogen sulfide (H_2S)

before the catalytic reaction starts. It is necessary to reduce the sulfur concentration in the feed gas to lower than 0.5 ppm in order to maintain adequate catalyst activity for a long period of time.

Some of the noteworthy commercial methanation processes include Comflux process, HICOM process, and Direct Methanation process.

The Comflux process is a Ni-based, pressurized fluidized bed (PFB) process converting carbon monoxide-rich gases into synthetic natural gas (CH_4) in a single stage, where both methanation and water gas shift reaction take place simultaneously. The HICOM process developed by British Gas Corporation is a fixed bed process, which involves a series of methanation stages using synthesis gas with a relatively low hydrogen- to-carbon monoxide ratio. Direct methanation is a process developed by Gas Research Institute (GRI), which methanates equimolar mixtures of H_2 and CO , producing CO_2 rather than H_2O (steam) in addition to methane:



The catalyst developed is claimed to be unsusceptible to sulfur poisoning, and as such, the process can be used to treat the raw, quenched gas from a coal gasifier with no or little pretreatment.

Higher Heating Value

The higher heating value (HHV; also known as the gross calorific value or gross energy) of a fuel is the amount of heat released during combustion by a specified quantity (initially at 25°C) and the products have returned to a temperature of 25°C .

The higher heating value takes into account the latent heat of vaporization of water in the combustion products, and is useful in calculating heating values for fuels where condensation of the reaction products is practical (e.g., in a gas-fired boiler used for space heat) and assumes all the water component is in liquid state at the end of combustion (in product of combustion).

See also: Heat Content, Lower Heating Value.

High-Temperature Water Splitting

High-temperature water splitting, a longer-term technology in the early stages of development, uses high temperatures to drive a series of chemical reactions that produce hydrogen from water. The chemicals are reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen. For both of the “thermo-chemical” processes described below, scientists have identified cycles appropriate to specific temperature ranges at which heat is available and are researching these systems in the laboratory.

A solar concentrator uses mirrors and a reflective or refractive lens to capture and focus sunlight to produce temperatures up to $2,000^\circ\text{C}$. Researchers have identified more than 150 chemical cycles that, in principle, could be used with heat from a solar concentrator to produce hydrogen; more than a dozen of these cycles are under active development.

One such pathway is the zinc/zinc oxide cycle, in which zinc oxide powder passes through a reactor that is heated by a solar concentrator operating at approximately $1,900^\circ\text{C}$ ($3,450^\circ\text{F}$). At this temperature, the zinc oxide dissociates to zinc and oxygen gas. The zinc is cooled, separated, and reacted with water to form hydrogen gas and solid zinc oxide. The zinc oxide can be recycled and reused to create more hydrogen.

Similarly, a nuclear reactor produces heat that can drive a series of chemical reactions to create hydrogen by splitting water and recycling the chemical constituents. The next-generation nuclear reactors under development could generate heat at temperatures of 800 to $1,000^\circ\text{C}$ ($1,470$ to $1,830^\circ\text{F}$). These temperatures are much lower than those produced by a solar concentrator, and as such, a different set of chemical reactions would be used to produce hydrogen.

The sulfur-iodine cycle is among the thermochemical cycles being investigated for this purpose. Sulfuric acid, when heated to approximately 850°C (1,560°F), decomposes to water, oxygen, and sulfur dioxide. The oxygen is removed, the sulfur dioxide and water are cooled, and the sulfur dioxide reacts with water and iodine to form sulfuric acid and hydrogen iodide. The sulfuric acid is separated and removed; the remaining hydrogen iodide is heated to 300°C (570°F), where it breaks down into hydrogen and iodine. The net result is hydrogen and oxygen, produced from water—the sulfuric acid and iodine are recycled and used to repeat the process.

See also: Hydrogen.

Homosphere

Below approximately 60 miles in altitude, the proportion of the major constituents in the atmosphere is very uniform and is known as the homosphere (the lower part of the atmosphere where the bulk gases are homogeneously mixed due to turbulent mixing or eddy diffusion), to distinguish it from the heterosphere above the approximate 60 miles of altitude, where the relative amounts of the major gaseous constituents change with height. In the homosphere there are sufficient atmospheric motions and a short enough molecular free path to maintain uniformity in composition. Above the boundary between the homosphere and the heterosphere (known as the homopause or the turbopause), the collision frequency (mean free path) of an individual molecule is sufficiently long to allow a partial separation (by gravity) of the (relatively) lighter (less dense) molecules from the heavier (more dense) constituents. Not surprisingly, the average molecular weight of the heterosphere decreases with height because the lighter (less dense) molecules dominate the composition at higher elevation.

See also: Atmosphere.

Horizontal and Vertical Axis Turbines

Both horizontal and vertical are applicable to applications such as tidal currents or river streams and are perceived as a critical element to hydrokinetic conversion concepts. Hydrokinetic energy conversion may employ either rotary turbo machinery or can use non-turbine schemes. While the former class (turbine system) encompasses various classical rotary technologies, the latter group (non-turbine system) is mostly based on various unconventional concepts. Such schemes include oscillating hydrofoil [30], vortex-induced vibration, piezo polymer conversion, and variable geometry sails.

Based on the alignment of the rotor axis with respect to water flow, three generic classes could be formed (i) horizontal axis, (ii) vertical axis, and (iii) cross flow turbines. The horizontal axis (alternately called as axial-flow) turbines have axes parallel to the fluid flow and employ propeller-type rotors. Inclined axis turbines have mostly been studied for small river energy converters. Horizontal axis turbines are common in tidal energy converters and are similar to modern-day wind turbines from concept and design point of view. Turbines with solid mooring structures require the generator unit to be placed near the riverbed or seafloor.

The cross flow turbines have rotor axes orthogonal to the water flow but parallel to the water surface (also known as floating waterwheels) are mainly drag-based devices and inherently less efficient than their lift-based counterparts. Darrieus turbines with cross flow arrangements may also fall under this category. Various arrangements under the vertical axis turbine category – in the vertical axis domain, Darrieus turbines are the most prominent options. The Gorlov turbine is another member of the vertical axis family, where the blades are of helical structure. Savonius turbines are drag-type devices, which may consist of straight or skewed blades.

Hydrokinetic turbines may also be classified based on their lift/drag properties, orientation to up/down flow, and fixed/variable (active/passive) blade pitching mechanisms. Different types of rotors may also be hybridized (such as, Darrieus–Savonius hybrid) in order to achieve certain performance features.

Hot Filtration Test

The hot filtration test (ASTM D4870) is a test to determine the stability (or instability) of a liquid fuel. An excess of sediment contained in residual fuels can cause many issues such as obstruction filters in pumps causing burner and engine systems to fail. Sediment can also accumulate on the bottom of storage tanks and cause issues with transfer pumps.

Thus, the test method is often used to examine the stability of a (conventional or alternative) fuel in which the fuel is hot-filtered to determine if solid particles exist in the fuel under the conditions of the test method.

The purpose of this test is to determine total sediment up to 0.40% m/m in residual fuel oils having a maximum viscosity of 55 centistokes at 100°C (212°F). There are some fuels that may exceed the maximum filtration time specified in this method due to factors beyond the presence of significant quantities of insoluble organic or inorganic material. The method may be used for the assessment of total sediment after regimes of fuel pretreatment designed to accelerate the aging process.

This method is performed by first starting the heating process on the filtration unit while conditioning filters. Once the filters are conditioned, they are weighed and placed on the instrument. In the next step, a beaker containing the residual fuel to be analyzed is weighed. The vacuum is then started, and the fuel oil is filtered and when the fuel has passed through the filters, they are rinsed with solvent to remove any fuel that is left so only sediment remains. The filters are then dried, cooled, and weighed. The sediment result is calculated as part of the whole sample.

See also: Bottom Sediment and Water.

Hot Gas Cleaning

When many biomass fuels are converted to gas, ash is entrained in to the gas stream. Before the gas is used, the ash must be removed to prevent slagging. Preferably, the removal should take place at the temperature of the hot gas (650 to 760°C, 1,200 to 1,400°F) so that heat is not lost during the process. The temperature at which the solids separation takes place can be lower, but it should be higher than 800 degrees F to prevent tar condensation.

Removing ash prior to combustion requires smaller solids separation equipment than would be necessary if the solids were removed after it is burned in a gas engine, gas boiler, or other energy conversion device, because the volume of gas is much greater following combustion. A smaller solids separation device is a significant advantage of gasification over direct combustion, because it can significantly reduce the costs of particulate matter emissions control.

See also: Gas Cleaning, Gas Processing, Gas Treatment.

Hot Potassium Carbonate Process

The hot potassium carbonate process has been utilized successfully for bulk removal of carbon dioxide from a number of gas mixtures. It has been used for sweetening natural gases containing both carbon dioxide and hydrogen sulfide. The process is not suitable for sweetening gas mixtures containing little or no carbon dioxide, as the potassium bisulfide should be difficult to regenerate if carbon dioxide is not present.

There are not only advantages to the use of this process, but there are also disadvantages. The advantages are: (i) it is a continuous circulating system employing an inexpensive chemical, (ii) it is an iso-thermal system in that both absorption and desorption of the acid gas are conducted at as nearly a uniform high temperature as can be obtained, thus requiring no heat exchange equipment in the fluid circulating system, and (iii) the desorption by stripping is accomplished with a smaller steam rate than required for an amine plant. On the negative side, the disadvantages are: (i) the process will not commercially reduce the hydrogen sulfide content to many pipeline specifications, (ii) the process is similar to other acid gas removal processes in that it is also prone to corrosion, and (iii) the process is also liable to problems relating to suspended solids and foaming.

The process using *potassium phosphate* is known as phosphate desulfurization, and it is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbon derivatives as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally.

See also: Alkali Washing Process, Gas Cleaning, Gas Processing, Gas Treatment.

Humidity

Humidity is a measure of the moisture contained in air, and the absolute humidity is a measure the amount of water in air while the relative humidity is a measure of the amount of water in air relative to the maximum amount of water the air could hold. The relative humidity increases with increasing water vapor or decreasing temperature. The dew point is the temperature at which air becomes saturated with moisture. More specifically, the absolute humidity measures the mass of water (grams) in a volume of air (cubic meters), essentially the density of water vapor (mass per volume). Thus, absolute humidity is expressed as g/m^3 (grams per cubic meter); in contrast, relative humidity is expressed as a percentage.

The absolute humidity of air varies with temperature; warm air contains more moisture than cold air, or to put it another way, warm air has higher water vapor density than an equivalent volume of cold air. Evaporation and condensation are occurring concurrently in any air mass, but one typically dominates. There is an increase in the volume of water vapor in a volume of air (absolute humidity) with increasing temperature.

Relative humidity measures the amount of moisture in air in comparison to the maximum volume of moisture the air would contain when saturated. Saturation represents the point where increasing vapor density results in condensation. Relative humidity increases if water is added to the air – adding water vapor increases the actual water vapor density.

Hybrid Poplars

Hybrid poplars are predominantly cottonwood trees and interspecific hybrids that have been selected and breed for fast growth. Sustained yields of 5 dry tons/acre/year have been documented in the north central United States and have reached 7 dry tons/acre/year on high productivity sites.

See also: Biomass, Wood.

Hydrane Process

The heart of the process is the Hydrane gasifier which is an example of a hydrogasifier which is fed with hydrogen and coal only, and the process might also be applicable to biomass feedstocks.

The hydrogen is produced in a separate unit by steam/oxygen gasification of unreacted char from the hydrogasifier. The Hydrane process was investigated by the U.S. Bureau of Mines (now incorporated in the Department of Energy) from 1955 up to the mid-1970s. The first reactor is a pretreatment stage in which the agglomerating properties of the coal are destroyed. Most American coals have been found to exhibit severe caking properties in high pressure hydrogen atmospheres at elevated temperatures, and coal agglomeration with concomitant plugging of reactors has consequently proved to be a major problem in the development of hydrogasifier units.

This problem is overcome in the Hydrane gasifier by partial gasification of the coal in the dilute-phase stage, where the particles react out of contact with each other. Wall temperatures have to be maintained above approximately $750^\circ C$ ($1,380^\circ F$) to prevent the coal particles from adhering to them. The gas/coal flow in the dilute-phase reactor allows devolatilization products to be cracked, and leaves the product gas relatively free of tars and oils.

In the Hydrane process, more than 90% of the methane produced is generated within the gasifier, thus minimizing the necessity for subsequent catalytic methanation processes. In the process, coal enters the gasifier and falls through a countercurrently flowing stream of hot gases rising from the second stage fluidized bed, therefore allowing

agglomerating coal to be hydrogasified (any agglomerating properties are usually destroyed during the preheating step). The preheated solids then enter the second zone (consisting of a bed fluidized by hydrogen) which permits maximum coal conversion without cracking the methane product to carbon.

The product gas requires purification and methanation so that the final product meets pipeline specifications. The char from the gasifier may be either completely consumed in synthesis gas production, or it may be used for power production.

See also: Hydrane Gasifier.

Hydrocarbon and Carbon Monoxide Controls

The emission of hydrocarbon derivatives and carbon monoxide will be caused by the incomplete combustion of the fuel for the boilers, furnaces, heaters, and diesel equipment used in oil shale plants. The control of external combustion sources such as boilers is primarily through proper design, operation, and maintenance.

Treating the flue gas from combustion sources for particulate or sulfur dioxide will also reduce hydrocarbon and carbon monoxide emissions. Other emissions of hydrocarbon derivatives will be caused by preheating raw shale prior to retorting and by storing crude shale oil and refined products.

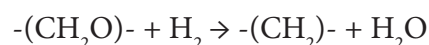
Storage tank emissions can be minimized by using floating-roof tanks, which can accommodate higher vapor pressures than cone-roof tanks without the need for venting.

See also: Carbon Monoxide, Gas Cleaning, Gas Processing, Gas Treatment, Hydrocarbons.

Hydrocarbon Fuels

Hydrocarbon derivatives, as such, are not usually produced from crops, there being insufficient amount of the hydrocarbon derivatives present in the plant tissue to make the process economical. However, biodiesel is produced from crops thereby offering an excellent renewable fuel for diesel engines.

The distillable oil obtained from the fast pyrolysis of biomass has high oxygen content. Ketone derivatives and aldehyde derivatives, carboxylic acid derivatives, ester derivatives, aliphatic and aromatic alcohol derivatives, and ether derivative have been detected in significant quantities. Because of the reactivity of oxygenated groups, the main problems of the oil are instability. The hydrodeoxygenation (HDO) of bio-oil in the presence of a cobalt molybdate catalyst was studied (Zhang et al., 2003), which is a most important route for upgrading the oil.



The reaction has strong analogies with typical refinery processes, such as the hydrodesulfurization and hydrodenitrogenation processes. In general, most of the hydrodeoxygenation studies have been performed using existing hydrodesulfurization catalysts (NiMo and CoMo on suitable carriers). However, these types of catalyst need activation using a suitable sulfur source and this is a major drawback when using low-to-no sulfur resources.

See also: Bio-oil.

Hydrocarbon Gases – Physical Constants

The number of carbon atoms in a member of the paraffin series determines whether the hydrocarbon will exist as a gas, a liquid, or a solid under standard conditions of temperature and pressure (STP' 60°F, 760 mm Hg) (Table H-4). Methane (CH_4) is a gas under all naturally occurring temperature and pressure conditions. Ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and its isomers are gaseous under standard surface conditions (Table) but may exist in either gaseous or liquid phase under the elevated temperature and pressure conditions found in subsurface reservoirs. On the other hand, members of the paraffin series with between 5 and 17 carbon atoms in their molecular structures (such as pentane, C_5H_{12} , hexane, C_6H_{14} , heptane, C_7H_{16} , octane, C_8H_{18}) are liquid under standard surface conditions and most temperature and pressure conditions encountered in subsurface reservoirs. Members of the paraffin series

with more than 17 carbon atoms are solid under most naturally occurring temperatures and pressures and when isolated from crude oil form the mixture known as paraffin wax.

Table H-4 Properties of gaseous (C_1 - C_4) paraffin hydrocarbons.

	Molecular	Boiling point	Density at 60°F	Density
Gas	weight	1 atm, °C (OF)	g/liter	Relative to air = 1
Methane	16.043	-161.5 (-258.7)	0.6786	0.5547
Ethylene	28.054	-103.7 (-154.7)	1.1949	0.9768
Ethane	30.068	-88.6 (-127.5)	1.2795	1.046
Propylene	42.081	-47.7 (-53.9)	1.8052	1.4757
Propane	44.097	-42.1 (-43.8)	1.8917	1.5464
1,2- Butadiene	54.088	10.9 (51.6)	2.3451	1.9172
1,3-Butadiene	54.088	-4.4 (24.1)	2.3491	1.9203
1-Butene	56.108	-6.3 (20.7)	2.4442	1.9981
cis-2-Butene	56.108	3.7 (38.7)	2.4543	2.0063
trans-2-Butene	56.108	0.9 (33.6)	2.4543	2.0063
iso-Butene	56.104	-6.9 (19.6)	2.4442	1.9981
n-Butane	58.124	-5.4 (31.1)	2.532	2.0698
iso-Butane	58.124	-11.7 (10.9)	2.5268	2.0656

Hydrocarbons

Hydrocarbons (hydrocarbon derivatives) are organic compounds which are composed of carbon and hydrogen only. The insertion of any non-carbon or non-hydrogen element in the molecule disqualifies that molecule from being a hydrocarbon.

The three simplest families of hydrocarbons are known as the alkanes, alkenes, and alkynes. Alkanes have the formula $C_n H_{2n+2}$ while alkenes have a double bond ($>C=C<$) in the molecule with the general formula $C_n H_{2n}$ and alkynes have a triple bond in the structure ($-C\equiv C-$) with the general formula $C_n H_{2n-2}$. The classifications for hydrocarbon are (i) saturated hydrocarbons, (ii) unsaturated hydrocarbons, and (iii) aromatic hydrocarbons.

Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon types and are composed entirely of single bonds that are saturated with hydrogen. The most general form of saturated hydrocarbons is $C_n H_{2n+2(1-r)}$, where r is the number of rings. Those with exactly one ring are the cycloalkanes. Unsaturated hydrocarbons (alkenes) have one or more double or triple bonds between carbon atoms. Those with one double bond have the formula $C_n H_{2n}$ (assuming they have a non-cyclic structure). Aromatic hydrocarbon derivatives (the arenes) hydrocarbons that have at least one aromatic ring in the molecule. The term aliphatic refers to non-aromatic hydrocarbons. Saturated aliphatic hydrocarbons are sometimes referred to as 'paraffins'. Aliphatic hydrocarbons containing a double bond between carbon atoms are sometimes referred to as olefins.

Hydrocarbon derivatives are also prevalent in nature. For example, there are certain species of flowering plants belonging to different families which convert a substantial amount of photosynthetic products into latex. The latex of such plants contains liquid hydrocarbon derivatives of high molecular weight (10,000). These hydrocarbon derivatives can be converted into high grade transportation fuel (i.e., crude oil). Therefore, hydrocarbon producing plants are called crude oil plants or petroplants and their crop as petrocrop. Natural gas is also one of the products obtained from hydrocarbon derivatives. Thus, crude oil plants can be a renewable resource for obtaining crude oil to be used in diesel engines. Normally, some of the latex-producing plants of families Euphorbiaceae, Apocynaceae, Asclepiadaceae,

Sapotaceae, Moraceae, Dipterocarpaceae, etc. are petroplants. Similarly, sunflower (family Compositae) and *Hardwickia pinnata* (family Leguminosae) are also petroplants. Some algae also produce hydrocarbon derivatives.

Different species of *Euphorbia* of family Euphorbiaceae serve as the petroplants that have the potential to be a renewable substitute for the conventional crude oil sources. The latex of *Euphorbia lathyris* contains fairly high percentage of terpenoids. These can be converted into high grade transportation fuel. Similarly, the carbohydrates (hexoses) from such plants can be used for ethanol formation.

Sugarcane (*Saccharum officinarum* - family Gramineae) is the main source of raw material for sugar industry. The wastes from sugar industry include bagasse, molasses, and press mud. After extracting the cane juice for sugar production, the cellulosic fibrous residue that remains is called bagasse. It is used as the raw material (biomass) and processed variously for the production of fuel, alcohols, single cell protein as well as in paper mills. Molasses is an important by-product of sugar mills and contains 50-55% fermentable sugars. One ton of molasses can produce approximately 280 liters of ethanol. Molasses is used for the production of animal feed, liquid fuel, and alcoholic beverages.

Sugar beet (*Beta vulgaris*, family-Chenopodiaceae) is yet another plant which contains a high percentage of sugars stored in fleshy storage roots. It is also an important source for production of sugar as well as ethanol.

Raising crops like sugarcane, sugar beet, tapioca, potato, maize, etc., purely for production of ethanol is described as energy cropping, and the crops are called energy crops. Cultivation of plants (trees) for obtaining fuel/fire wood is described as energy plantation. Other plants, such as Euphorbiaceae plants like *Euphorbia lathyris*, milkweed (*Asclepias speciosa*) and the tree legume *Copaifera multijuga*, produce hydrocarbon derivatives which can be converted into and used as diesel. In addition, some freshwater and marine algae are also known to accumulate hydrocarbon derivatives. Some algae like Chlamydomonas and anaerobic bacteria like Clostridium produce hydrogen gas, which can be used as a pollution free fuel. Long-term research efforts are needed to develop these organisms as sources of bioenergy.

The euphorbeans and milkweeds can be grown in relatively dry environments on lands not suited for crop production; this makes them highly attractive sources of biofuels. The Euphorbias are relatives of plants used to produce rubber; they produce a latex, which has approximately 30% hydrocarbon derivatives emulsified in water.

However, hydrocarbon derivatives, as such, are not usually produced from crops, there being an insufficient amount of the hydrocarbon derivatives present in the plant tissue to make the process economical. However, biodiesel is produced from crops thereby offering an excellent renewable fuel for diesel engines.

There are certain species of flowering plants belonging to different families which convert a substantial amount of photosynthetic products into latex. The latex of such plants contains liquid hydrocarbon derivatives of high molecular weight (10,000). These hydrocarbon derivatives can be converted into high-grade transportation fuel (i.e., petroleum). Therefore, hydrocarbon-producing plants are called petroleum plants or petroplants and their crop as petrocrop. Natural gas is also one of the products obtained from hydrocarbon derivatives. Thus, petroleum plants can be an alternative source for obtaining petroleum to be used in diesel engines. Normally, some of the latex-producing plants of families Euphorbiaceae, Apocynaceae, Asclepiadaceae, Sapotaceae, Moraceae, and Dipterocarpaceae are petroplants. Similarly, sunflower (family Compositae) and *Hardwickia pinnata* (family Leguminosae) are also petroplants. Some algae also produce hydrocarbon derivatives.

Different species of *Euphorbia* of family Euphorbiaceae serve as the petroplants that have the potential to be a renewable substitute for the conventional petroleum sources. Latex of *Euphorbia lathyris* contains a fairly high percentage of terpenoids. These can be converted into high-grade transportation fuel. Similarly, the carbohydrates (hexoses) from such plants can be used for ethanol formation.

Sugarcane (*Saccharum officinarum* - family Gramineae) is the main source of raw material for sugar industry. The wastes from sugar industry include bagasse, molasses, and press mud. After extracting the cane juice for sugar production, the cellulosic fibrous residue that remains is called bagasse. It is used as the raw material (biomass) and processed variously for the production of fuel, alcohols, single cell protein as well as in paper mills. Molasses is an important by-product of sugar mills and contains 50-55% fermentable sugars. One ton of molasses can produce approximately 280 liters of ethanol. Molasses is used for the production of animal feed, liquid fuel, and alcoholic beverages.

Sugar beet (*Beta vulgaris*, family Chenopodiaceae) is yet another plant which contains a high percentage of sugars stored in fleshy storage roots. It is also an important source for production of sugar as well as ethanol.

Raising crops like sugarcane, sugar beet, tapioca, potato, maize, etc., purely for production of ethanol is described as energy cropping, and the crops are called energy crops. Cultivation of plants (trees) for obtaining fuel/fire wood is described as energy plantation.

Other plants, such as Euphorbiaceae plants like *Euphorbia lathyris*, milkweed (*Asclepia speciosa*), and the tree legume *Copaifera multijuga*, produce hydrocarbon derivatives which can be converted into and used as diesel, called biodiesel. In addition, some freshwater and marine algae are also known to accumulate hydrocarbon derivatives. Some algae like *Chlamydomonas* and anaerobic bacteria like *Clostridium* produce hydrogen gas, which can be used as a pollution-free fuel. Long-term research efforts are needed to develop these organisms as sources of bioenergy.

The euphorbeans and milkweeds can be grown in relatively dry environments on lands not suited for crop production; this makes them highly attractive sources of biofuels. The Euphorbias are relatives of plants used to produce rubber; they produce a latex, which has approximately 30% hydrocarbon derivatives emulsified in water.

However, hydrocarbon derivatives, as such, are not usually produced from crops, there being an insufficient amount of the hydrocarbon derivatives present in the plant tissue to make the process economical. However, biodiesel is produced from crops thereby offering an excellent renewable fuel for diesel engines.

See also: Biomass, Crops, Hydrocarbons.

Hydrocracking

Hydrocracking (hydroconversion) is a catalytic high-pressure high-temperature process for the conversion of a variety of feedstocks (including bio-oil) in the presence of fresh and recycled hydrogen; carbon-carbon bonds are cleaved in addition to the removal of heteroatom species. Like hydrotreating, hydrocracking also falls under the general umbrella of hydroprocessing. The outcome is the conversion of a variety of feedstocks to a range of products, and units to accomplish this goal can be found at various points in a refinery.

Hydrocracking is a more recent process development compared to the older thermal cracking, visbreaking, and coking. In fact, the use of hydrogen in thermal processes is perhaps the single most significant advance in refining technology during the twentieth century and the ability of refiners to cope with the renewed trend toward distillate production from heavier feedstocks with low atomic hydrogen/carbon ratios has created a renewed interest in hydrocracking. Without the required conversion units, heavier crude oils produce in lower yields of naphtha and middle distillate. To maintain current gasoline and middle distillate production levels, additional conversion capacity is required because of the differential in the amount of distillates produced from conventional (low-density or conventional) crude oil and the distillate products produced from heavier crude oil.

The concept of hydrocracking allows the refiner to produce products having a lower molecular weight with higher hydrogen content and a lower yield of coke. In summary, hydrocracking facilities add flexibility to refinery processing and to the product slate. Hydrocracking is more severe than hydrotreating there being the intent, in hydrocracking processes, to convert the feedstock to lower-boiling products rather than to treat the feedstock for heteroatom and metals removal only.

Hydrocracking is an extremely versatile process that can be utilized in many different ways, and one of the advantages of hydrocracking is its ability to break down high-boiling aromatic stocks produced by catalytic cracking or coking (Figure H-1).

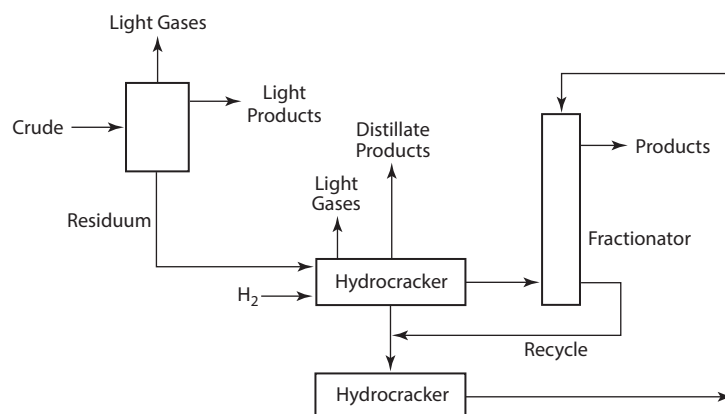


Figure H-1 Single-stage and double-stage hydrocracking.

To take full advantage of hydrocracking, the process must be integrated in the refinery with other process units. In gasoline production, for example, the hydrocracker product must be further processed in a catalytic reformer as it has a high naphthene content and relatively low octane number. The high naphthene content makes the hydrocracker gasoline an excellent feed for catalytic reforming, and good yields of high-octane-number gasoline can be obtained.

If high-molecular-weight petroleum fractions are pyrolyzed, that is, if no hydrogenation occurs, progressive cracking and condensation reactions generally lead to the final products. These products are usually (i) gaseous and low-boiling liquid compounds of high hydrogen content, and/or (ii) liquid material of intermediate molecular weight with a hydrogen-carbon atomic ratio differing more or less from that of the original feedstock, depending on the method of operation, and/or (iii) material of high molecular weight, such as coke, possessing a lower hydrogen-carbon atomic ratio than the starting material.

Highly aromatic or refractory recycle stocks or gas oils that contain varying proportions of highly condensed aromatic structures (for example, naphthalene and phenanthrene) usually crack, in the absence of hydrogen, to yield intractable residues and coke.

An essential difference between pyrolysis (thermal decomposition, usually the absence of any added agent) and hydrogenolysis (thermal decomposition in the presence of hydrogen and a catalyst or a hydrogen-donating solvent) of petroleum is that in pyrolysis, a certain amount of polymerized heavier products, like cracked residuum and coke, is always formed along with the low-boiling products, such as gas and naphtha (a gasoline precursor). During hydrogenolysis (destructive hydrogenation), polymerization may be partly or even entirely prevented so that only low-boiling products are formed. The prevention of coke formation usually results in an increased distillate (e.g., gasoline) yield. Depending on the feedstock being processed and the type of plant design employed (single-stage or two-stage), flexibility can be provided to vary product distribution.

Though several technologies exist to upgrade high-boiling feedstocks, selection of the optimum process units is very much dependent on the requirements and goals of each refinery, with the market pull being the prime motivator. Furthermore, processing options systems to dig deeper into the barrel by converting more of the higher boiling materials to distillable products should not only be cost-effective and reliable, but also flexible.

Hydrocracking adds that flexibility and offers the refiner a process that can handle varying feeds and operate under diverse process conditions. Utilizing different types of catalysts can modify the product slate produced. Reactor design and the number of processing stages play a role in this flexibility. Finally, in relation to the conversion measures for upgrading processes. Such measures are necessary for any conversion process but more particularly for hydrocracking processes where hydrogen management is an integral, and essential, part of process design.

The objective of any upgrading process is to convert high-boiling feedstocks into marketable products by reducing their heteroatom (nitrogen, oxygen, and sulfur) and metal contents, modifying the structures of the asphaltene constituents (reducing coke precursors), and converting the high-molecular-weight polar species large molecules into lower-molecular-weight and lower-boiling hydrocarbon products. Upgrading processes are evaluated on the basis of liquid yield (i.e., naphtha, distillate and gas oil), heteroatom removal efficiency, feedstock conversion (FC), carbon mobilization (CM), and hydrogen utilization (HU), along with other process characteristics. Definition of FC, CM, and HU are:

$$FC = (\text{Feedstock}_{\text{IN}} - \text{Feedstock}_{\text{OUT}}) / \text{Feedstock}_{\text{IN}} \times 100$$

$$CM = \text{Carbon}_{\text{LIQUIDS}} / \text{Carbon}_{\text{FEEDSTOCK}} \times 100$$

$$HU = \text{Hydrogen}_{\text{LIQUIDS}} / \text{Hydrogen}_{\text{FEEDSTOCK}} \times 100$$

High carbon mobilization (CM <100%) and high hydrogen utilization (HU) correspond to high feedstock conversion (RC) processes involving hydrogen addition such as hydrocracking. Since hydrogen is added, hydrogen utilization can be greater than 100%. These tasks can be achieved by using thermal and/or catalytic processes. Low carbon mobilization and low hydrogen utilization correspond to low feedstock conversion such as coking (carbon rejection) processes. Maximum efficiency from an upgrading process can be obtained by maximizing the liquid yield

and its quality by minimizing the gas (C_1 - C_4) yield, simultaneously. Under these operating conditions the hydrogen consumption would be the most efficient, i.e., hydrogen is consumed to increase the liquid yield and its quality. Several process optimization models can be formulated if the reaction kinetics is known.

Hydrocracking generates air emissions through process heater flue gas, vents, and fugitive emissions. Unlike fluid catalytic cracking catalysts, hydrocracking catalysts are usually regenerated off-site after months or years of operations, and little or no emissions or dust are generated. However, the use of heavy crude oil as feedstock to the unit can change this balance.

Hydrocracking produces less sour wastewater than catalytic cracking. Hydrocracking, like catalytic cracking, produces sour wastewater at the fractionator. These processes include processing in a separator (API separator, corrugated plate interceptor) that creates a sludge. Physical or chemical methods are then used to separate the remaining emulsified oils from the wastewater. Treated wastewater may be discharged to public wastewater treatment, to a refinery secondary treatment plant for ultimate discharge to public wastewater treatment, or may be recycled and used as process water. The separation process permits recovery of usable oil, and also creates a sludge that may be recycled or treated as a hazardous waste.

In addition, oily sludge from the wastewater treatment facility that results from treating sour wastewaters may be hazardous wastes (unless they are recycled in the refining process). These include API separator sludge, primary treatment sludge, sludge from various gravitational separation units, and float from dissolved air flotation units.

See also: Hydrocracking Catalysts, Hydrocracking Chemistry, Hydrocracking Processes, Hydroprocessing, Hydrotreating, Refining.

Hydrocracking Catalysts

Hydrocracking catalysts typically contain separate hydrogenation and cracking functions. Palladium sulfide and promoted group VI sulfides (nickel molybdenum or nickel tungsten) provide the hydrogenation function. These active compositions saturate aromatics in the feed, saturate olefins formed in the cracking, and protect the catalysts from poisoning by coke. Zeolites or amorphous silica-alumina provide the cracking functions. The zeolites are usually type Y (faujasite), ion exchanged to replace sodium with hydrogen and make up 25 to 50% of the catalysts. Pentasils (silicalite or ZSM-5) may be included in dewaxing catalysts.

Hydrocracking catalysts, such as nickel (5% by weight) on silica-alumina, work best on feedstocks that have been hydrofined to low nitrogen and sulfur levels. The nickel catalyst then operates well at 350 to 370°C (660 to 700°F) and a pressure of approximately 1,500 psi to give good conversion of feed to lower-boiling liquid fractions with minimum saturation of single-ring aromatics and a high iso-paraffin-to-n-paraffin ratio in the lower- molecular-weight paraffins.

The poisoning effect of nitrogen can be offset to a certain degree by operation at a higher temperature. However, the higher temperature tends to increase the production of material in the methane (CH_4) to butane (C_4H_{10}) range and decrease the operating stability of the catalyst so that it requires more frequent regeneration. Catalysts containing platinum or palladium (approximately 0.5% wet) on a zeolite base appear to be somewhat less sensitive to nitrogen than are nickel catalysts, and successful operation has been achieved with feedstocks containing 40 ppm nitrogen. This catalyst is also more tolerant of sulfur in the feed, which acts as a temporary poison, the catalyst recovering its activity when the sulfur content of the feed is reduced.

On such catalysts as nickel or tungsten sulfide on silica-alumina, isomerization does not appear to play any part in the reaction, as uncracked normal paraffins from the feedstock tend to retain their normal structure. Extensive splitting produces large amounts of low-molecular-weight (C_3 - C_6) paraffins, and it appears that a primary reaction of paraffins is catalytic cracking followed by hydrogenation to form iso-paraffins. With catalysts of higher hydrogenation activity, such as platinum on silica-alumina, direct isomerization occurs. The product distribution is also different, and the ratio of low- to intermediate-molecular-weight paraffins in the breakdown product is reduced.

In addition to the chemical nature of the catalyst, the physical structure of the catalyst is also important in determining the hydrogenation and cracking capabilities, particularly for high-boiling feedstocks. When gas oils and residua are used, the feedstock is present as liquids under the conditions of the reaction. Additional feedstock and

the hydrogen must diffuse through this liquid before reaction can take place at the interior surfaces of the catalyst particle.

At high temperatures, the reaction rates can be much higher than diffusion rates and concentration gradients can develop within the catalyst particle. Therefore, the choice of catalyst porosity is an important parameter. When feedstocks are to be hydrocracked to liquefied petroleum gas and gasoline, pore diffusion effects are usually absent. High surface area (approximately 300 m²/g) and low-to-moderate porosity. With reactions involving high-molecular-weight feedstocks, pore diffusion can exert a large influence, and catalysts with pore diameters greater than 80 Å are necessary for more efficient conversion.

Precious metal catalysts, particularly catalysts incorporating platinum or platinum and palladium, are used in the latter stages of deep-desulfurization process. They have excellent performance in hydrogenation of monocyclic aromatic hydrocarbon derivatives and are likely to become more and more important in the years ahead, and refiners seek to hydrocrack higher amounts of the high-boiling feedstocks. Current efforts are seeking to produce such catalysts with increased hydrogenation activity as well as resistance to sulfur and nitrogen poisoning while balancing these characteristics. In addition, work is being done to assign appropriate cracking activity to match specific applications using inorganic (composite) oxides, such as amorphous alumina, silica alumina, or crystalline silica alumina, as carriers and optimization of the amount of the precious metals and highly-dispersed metal impregnation methods.

The cobalt-molybdenum, nickel-molybdenum, and precious metal catalysts are also available for use in deep desulfurization and aromatics hydrogenation. These catalysts should be helpful in producing diesel fuel with a sulfur content of 50 ppm or less only by substituting catalysts. The bimetallic catalyst in the reaction mix promotes (i) formation of an olefin, (ii) hydrogenation of fragments, and (iii) prevents condensation reactions which lead to catalyst fouling.

Hydrocracking Chemistry

Hydrogen is consumed in all hydrocracking reactions. Carbon-carbon bonds in feedstock constituents are broken and the fragments hydrogenated to form lower-molecular-weight products. Polycyclic aromatics are partially saturated and ring opening in one or more places follows – at least one ring is usually retained. Dual function catalysts containing both acid activity and hydrogenation-dehydrogenation activity are required.

Hydrocracking reactions are initiated by partial dehydrogenation over the metallic components in the catalyst to form an olefin; of course, it is in a low concentration and is rapidly adsorbed on an acid site and converted to carbonium ion cracks (usually in the β -position) to form two fragments that may undergo further cracking, but at some critical molecular weight, they become hydrogenated, and desorbed from the catalyst and constitute final product.

The chemistry of hydrocracking is basically similar to that of catalytic cracking, but with concurrent hydrogenation. The catalyst assists in the production of carbonium ions via olefin intermediates, and these intermediates are quickly hydrogenated under the high-hydrogen partial pressures employed in hydrocracking. The rapid hydrogenation prevents adsorption of olefins on the catalyst and, hence, prevents their subsequent dehydrogenation, which ultimately leads to coke formation so that long on-stream times can be obtained without the necessity of catalyst regeneration.

One of the most important reactions in hydrocracking is the partial hydrogenation of polycyclic aromatics followed by rupture of the saturated rings to form substituted monocyclic aromatics. The side chains may then be split off to give iso-paraffins. It is desirable to avoid excessive hydrogenation activity of the catalyst so that the monocyclic aromatics become hydrogenated to naphthenes; furthermore, repeated hydrogenation leads to loss in octane number, which increases the catalytic reforming required to process the hydrocracked naphtha.

Side chains of three or four carbon atoms are easily removed from an aromatic ring during catalytic cracking, but the reaction of aromatic rings with shorter side chains appears to be quite different. For example, hydrocracking single-ring aromatics containing four or more methyl groups produces largely iso-butane and benzene. It may be that successive isomerization of the feed molecule adsorbed on the catalyst occurs until a four-carbon side chain is formed, which then breaks off to yield iso-butane and benzene. Overall, coke formation is low in hydrocracking

since the secondary reactions and the formation of the precursors to coke are suppressed as the hydrogen pressure is increased.

It is the physical and chemical composition of a feedstock that plays a large part not only in determining the nature of the products that arise from refining operations but also in determining the precise manner by which a particular feedstock should be processed. Furthermore, it is apparent that the conversion of heavy crude oils and residua requires new lines of thought to develop suitable processing scenarios. Indeed, the use of thermal (carbon rejection) processes and of hydrothermal (hydrogen addition) processes, which were inherent in the refineries designed to process low-boiling feedstocks, has been a particular cause for concern. This has brought about the evolution of processing schemes that accommodate the heavier feedstocks. As a point of reference, an example of the former option is the delayed coking process in which the feedstock is converted to overhead with the concurrent deposition of coke, for example that used by Suncor, Inc., at their oil sands plant.

Hydrocracking Processes

There are three basic flow schemes for hydrocracking processes which are (i) single-stage, (ii) two-stage, and (iii) series flow, although there are many modifications of each but pertinent features (Figure H-1). The choice of flow scheme depends upon the feedstock, the desired products, and the flexibility that is chosen for the process.

In the single-stage system, fresh feedstock along with recycled hydrogen is heated to the desired reaction temperature, and then contacted with catalyst in the reactor. Hydrocracking reactions are exothermic, and to control temperatures in the desired range, conversion per pass can be limited or cooling with quench recycle gas can be used. The reactor effluent is heat-exchanged and passed to a high-pressure separator. Hydrogen and high pressure separator liquid are flashed into a low-pressure drum where most of the dissolved gases are removed from the normal liquid product. The flash drum liquid is fed to a fractionator for separation into the desired products. Fractionator bottoms boiling range of the products can be recycled for complete conversion.

In the two-stage system, there are two complete reactor stages, each containing a charge pump, recycle compressor, heat exchangers, heater, reactor, cooler, and high-pressure fractionator. The first stages are separated by the stripper or fractionator. The first-stage reactor decomposes nitrogen and sulfur compounds, saturates olefins, and partially saturates polycyclic aromatics. The stripper or fractionator removes H₂S, NH₃, and other low-boiling gases, leaving a mixture of paraffins, naphthenes, and aromatics essentially free from impurities. The second stage processes the cleaned feedstock and converts it into the desired boiling range products. This system is the most versatile of the two-reactor schemes as regards variety of charge stocks and products which can be accommodated. A large number of such units are on stream for processing feedstocks such as high-boiling as vacuum gas oil and propane-deasphalted gas oils to produce naphtha, kerosene, and distillates.

The series-flow two-reactor system is similar to the one-reactor system except that there are two reactors in series, as shown, each containing a different catalyst. The first reactor performs the same function as the first reactor in the two-stage scheme. The second reactor carries out the hydrocracking reactions in the presence of hydrogen sulfide and ammonia. This scheme has the advantage of being more economical to build and operate in some instances.

The reactor effluent is cooled through a variety of heat exchangers including the feed-effluent exchanger and one or more air coolers. De-aerated condensate is injected into the first-stage reactor effluent before the final air cooler in order to remove ammonia and some of the hydrogen sulfide. This prevents solid ammonium disulfide from depositing in the system. A body of expertise in the field of materials selection for hydrocracker cooling trains is quite important for proper design.

The reactor effluent leaving the air cooler is separated into hydrogen-rich recycle gas, a sour water stream, and a hydrocarbon liquid stream in the high-pressure separator. The sour water effluent stream is often then sent to a plant for ammonia recovery and for purification so water can be recycled back to the hydrocracker. The hydrocarbon rich stream is pressure reduced and fed to the distillation section after low-boiling products are flashed off in a low-pressure separator. The hydrogen-rich gas stream from the high-pressure separator is recycled back to the reactor feed by using a recycle compressor. Sometimes with sour feeds, the first-stage recycle gas is scrubbed with an amine system to remove hydrogen. If the feed sulfur level is high, this option can improve the performance of the catalyst and result in less costly materials of construction.

Overall, a single-stage once-through (SSOT) unit resembles the first stage of the two-stage plant. This type of hydrocracker usually requires the least capital investment. The feedstock is not completely converted to low-boiling products. For this application, the refiner must have a demand for highly refined heavy crude oil. In many refining situations, such an oil product can be used as lube oil plant feed or as FCC plant feed or in low sulfur oil blends or as ethylene plant feed. It also lends itself to stepwise construction of a future two-stage hydrocracker for full feed conversion.

A single-stage recycle (SSREC) unit converts heavy crude oil completely into low-boiling products with a flow scheme resembling the second stage of the two-stage plant. Such a unit maximizes the yield of naphtha, jet fuel, or diesel depending on the recycle cut point used in the distillation section. This type of unit is more economical than the more complex two-stage unit when plant design capacity is less than approximately 10,000 to 15,000 bbl/day. Commercial SSRFC plants have operated to produce low pour point diesel fuel from waxy Middle East vacuum gas oils. Recent emphasis has been placed on the upgrading of low-boiling gas oils into jet fuels.

Building on the theme of one- or two-stage hydrocracking, the once-through partial conversion (OTPC) concept evolved. This concept offers the means to convert high-boiling vacuum gas oil feed into high quality gasoline, jet fuel, and diesel products by a partial conversion operation. The advantage is lower initial capital investment and also lower utilities consumption than a plant designed for total conversion. Because total conversion of the higher molecular weight compounds in the feedstock is not required, once-through hydrocracking can be carried out at lower temperatures and in most cases at lower hydrogen partial pressures than in recycle hydrocracking, where total conversion of the feedstock is normally an objective.

One disadvantage of once-through hydrocracking compared to a recycle operation is a somewhat reduced flexibility for varying the ratio of gasoline to middle distillate that is produced. A greater quantity of naphtha can be produced by increasing conversion, and production of jet fuel plus diesel can also be increased. But selectivity for higher boiling products is also a function of conversion. Selectivity decreases as once-through conversion increases. If conversion is increased too much, the yield of desired product will decrease, accompanied by an increase in gas production and the production of other low-boiling products. Higher yields of naphtha or kerosene are possible from a recycle operation rather than from a once-through operation.

See also: Bio-oil, Refining.

Hydrodenitrogenation

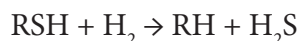
Many types of biomass contain alkaloids and other forms of nitrogen-containing species. The nitrogen, which can be a serious disadvantage in fuels, must be removed from the bio-oil, and this is achieved by a process known as hydrodenitrogenation which is the removal of nitrogen by hydrotreating.

Hydrodenitrogenation is more difficult to accomplish than hydrodesulfurization, but the relatively smaller amounts of nitrogen-containing compounds in conventional crude oil made this of little concern to refiners. However, the trend to heavier feedstocks in refinery operations, which are richer in nitrogen than the conventional feedstocks, has increased the awareness of refiners to the presence of nitrogen compounds in crude feedstocks. For the most part, however, hydrodesulfurization catalyst technology has been used to accomplish hydrodenitrogenation although such catalysts are not ideally suited to nitrogen removal. Limitations of hydrodesulfurization catalysts when applied to hydrodenitrogenation have been recognized, and there are reports of attempts to manufacture catalysts more specific to nitrogen removal.

See also: Hydrodesulfurization.

Hydrodesulfurization

Hydrodesulfurization is the removal of sulfur from feedstocks, such as shale oil, by the use of hydrogen and a catalyst.





The reactor design commonly used in hydrodesulfurization of distillates is the fixed-bed reactor design in which the feedstock enters at the top of the reactor and the product leaves at the bottom of the reactor.

The catalyst remains in a stationary position (fixed-bed) with hydrogen and petroleum feedstock passing in a downflow direction through the catalyst bed. The hydrodesulfurization reaction is exothermic, and the temperature rises from the inlet to the outlet of each catalyst bed. With a high hydrogen consumption and subsequent large temperature rise, the reaction mixture can be quenched with cold recycled gas at intermediate points in the reactor system. This is achieved by dividing the catalyst charge into a series of catalyst beds, and the effluent from each catalyst bed is quenched to the inlet temperature of the next catalyst bed.

The extent of desulfurization is controlled by raising the inlet temperature to each catalyst bed to maintain constant catalyst activity over the course of the process. Fixed-bed reactors are mathematically modeled as plug-flow reactors with little back mixing in the catalyst beds. The first catalyst bed is poisoned with vanadium and nickel at the inlet to the bed and may be a cheaper catalyst (guard bed). As the catalyst is poisoned in the front of the bed, the temperature exotherm moves down the bed and the activity of the entire catalyst charge declines thus requiring a raise in the reactor temperature over the course of the process sequence. After catalyst regeneration, the reactors are opened and inspected, and the high metal content catalyst layer at the inlet to the first bed may be discarded and replaced with fresh catalyst. The catalyst loses activity after a series of regenerations and, consequently, after a series of regenerations, it is necessary to replace the complete catalyst charge. In the case of feedstocks with a high metal content, it is often necessary to replace the entire catalyst charge rather than to regenerate it. This is due to the fact that the metal contaminants cannot be removed by economical means during rapid regeneration, and the metals have been reported to interfere with the combustion of carbon and sulfur, catalyzing the conversion of sulfur dioxide (SO_2) to sulfate (SO_4^{2-}) that has a permanent poisoning effect on the catalyst.

Fixed-bed hydrodesulfurization units are generally used for distillate hydrodesulfurization and may also be used for residuum hydrodesulfurization but require special precautions in processing. The residuum must undergo two-stage electrostatic desalting so that salt deposits do not plug the inlet to the first catalyst bed, and the residuum must be low in vanadium and nickel content to avoid plugging the beds with metal deposits. Hence, the need for a guard bed in residuum hydrodesulfurization reactors.

During the operation of a fixed-bed reactor, contaminants entering with fresh feed are filtered out and fill the voids between catalyst particles in the bed. The buildup of contaminants in the bed can result in the channeling of reactants through the bed and reducing the hydrodesulfurization efficiency. As the flow pattern becomes distorted or restricted, the pressure drop throughout the catalyst bed increases. If the pressure drop becomes high enough, physical damage to the reactor internals can result. When high-pressure drops are observed throughout any portion of the reactor, the unit is shut down and the catalyst bed is skimmed and refilled.

With fixed-bed reactors, a balance must be reached between reaction rate and pressure drop across the catalyst bed. As catalyst particle size is decreased, the desulfurization reaction rate increases but so does the pressure drop across the catalyst bed. Expanded-bed reactors do not have this limitation, and small 1/32 inch (0.8 mm) extrudate catalysts or fine catalysts may be used without increasing the pressure drop.

See also: Fixed-Bed Process, Fixed-Bed Reactor or Moving-Bed Reactor, Refining.

Hydrodesulfurization Catalysts

Hydrodesulfurization catalysts consist of metals impregnated on a porous alumina support. Almost all of the surface area is found in the pores of the alumina (200 to 300 m^2/g), and the metals are dispersed in a thin layer over the entire alumina surface within the pores. This type of catalyst does display a huge catalytic surface for a small weight of catalyst. Cobalt (Co), molybdenum (Mo), and nickel (Ni) are the most commonly used metals for desulfurization catalysts. The catalysts are manufactured with the metals in an oxide state. In the active form, they are in the sulfide state, which is obtained by sulfiding the catalyst either prior to use or with the feed during actual use. Any catalyst

that exhibits hydrogenation activity will catalyze hydrodesulfurization to some extent. However, the Group VIB metals (chromium, molybdenum, and tungsten) are particularly active for desulfurization, especially when promoted with metals from the iron group (iron, cobalt, and nickel).

Hydroelectric Dams

Dams have existed for thousands of years. The oldest known dam, the Sadd el-Kafara (Arabic for “Dam of the Pagans”), was constructed over 4,500 years ago twenty miles south of Cairo, Egypt. The 348-foot wide, 37-foot high dam was constructed to create a reservoir in the Wadi el-Garawi. The dam was built with limestone blocks, set in rows of steps approximately eleven inches high. It appears that the dam was supposed to be used to create a reservoir that would supply drinking water for people and animals working in a nearby quarry. Scientists and archaeologists believe that the Sadd el-Kafara failed after only a few years of use because there is no evidence of siltation at the remains of the dam. When water flows into the reservoir created by a dam, the silt—sand and other debris carried with the stream—is allowed to settle, rather than be borne further downstream by the force of the flow of a stream or river. In the still water behind a dam, this sediment is deposited on the bottom of the reservoir.

The earliest dams were built for utilitarian purposes, to create reservoirs for drinking supplies—as in the Sadd el-Kafara—or to prevent flooding or for irrigation purposes. Early dams were even used to create lakes for recreational purposes. In the middle of the first century, the Roman emperor, Nero, constructed three dams to create three lakes to add to the aesthetic beauty of his villa.

Currently, a variety of dam structures are utilized which can be classified as either (i) embankment dams or (ii) concrete dams. Embankment dams are constructed with locally available natural resources. There are several different types of embankment dams, including earth dams—which are constructed primarily of compacted earth; tailings dams—constructed from mine wastes; and rockfill dams—which are constructed with dumped or compacted rock. The shape of these dams is usually dependent on the natural settling angle of the materials used to build them. Concrete, bitumen, or clay is often used to prevent water from seeping through the dam. This can be in the form of a thin layer of concrete or bitumen facing which acts as a seal, or in the form of a central core wall of clay or other fine materials constructed within the dam, allowing water to penetrate the upstream side of the structure, but preventing it from moving beyond the clay core.

Concrete dams are more permanent structures than embankment dams. Concrete dams can be categorized as gravity, arch, or buttress. Because concrete is a fairly expensive material, different construction techniques were developed to reduce the quantity of concrete needed. This is highly dependent upon geological considerations. In particular, the rock foundations must be able to support the forces imposed by the dam, and the seismic effects of potential earthquakes. Gravity dams work by holding water back by way of their own weight. A gravity dam can be described as a long series of heavy vertical, trapezoidal structural elements firmly anchored at the base. It is generally a straight wall of masonry that resists the applied water-pressure by its sheer weight. The strength of a gravity dam ultimately depends on its weight and the strength of its base.

An arch dam, on the other hand, relies on its shape to withstand the pressure of the water behind it. The arch curves back upstream, and the force exerted by the water is transferred through the dam into the river valley walls and to the river floor. They are normally constructed in deep gorges where the geological foundations are very sound. The Hoover Dam in the United States is an example of a concrete arch dam.

The buttress dam uses much less concrete than the gravity dam, and also relies on its shape to transfer the water load. Buttress dams were developed in areas where materials were scarce or expensive, but labor was available and cheap. They have been built primarily for purposes of irrigation. The dams are particularly suited for wide valleys. They have a thin facing supported at an incline by a series of buttresses. The buttresses themselves come in a variety of shapes, including the multiple arch and the simple slab deck (see Figure 3). The weight of the concrete is transferred to bedrock through the downstream legs or “buttresses” of the structure. The Coolidge Dam near Globe, Arizona is an example of a buttress dam, constructed of three huge domes of reinforced concrete.

Using water as a source of power actually dates back more than 2,000 years when the Greeks used water to turn wheels to grind wheat into flour. The first recorded use of water power was a clock, built around 250 B.C.E., and since that time, falling water has provided power to grind corn, wheat, and sugar cane, as well as to saw mills. In the tenth

century, water wheels were used extensively in the Middle East for milling and irrigation. One of these dams, built at Dizful (Iran), raised the water 190 feet and supplied the residents with water to grind corn and sugar cane.

The discoveries associated with electromagnetism in the early nineteenth century had a major impact on the development of hydropower. The development of electric power generators and the fact that electric power was the only form of energy in a “ready to use” state which can be transmitted over long distances have been particularly significant to hydroelectricity. Dams located away from population centers could be useful generators if there was a way to supply the consumers. Water turbines were also developed during the nineteenth century as a natural successor to the water wheel. The high performance and small size of the turbine relative to the water wheel were important advancements. Combining the technology of electric generators, turbines, and dams resulted in the development of hydroelectric power.

Water was first used to generate electricity in 1880 in Grand Rapids, Michigan when a water turbine was used to provide storefront lighting to the city. In 1882—only two years after Thomas Edison demonstrated the incandescent light bulb—the first hydroelectric station to use Edison’s system was installed on the Fox River at Appleton, Wisconsin. In 1881, construction began on the first hydroelectric generating station on the Niagara River in Niagara Falls on the New York-Canadian border. For twenty years, this project met the small electricity needs of the city. Water from the upper Niagara River fell 86 feet down a flume (a narrow gorge with a stream running through it) onto spinning water wheels on the lower river to generate electricity. The electricity was used to run the equipment of a paper company, other small factories, and sixteen open arc-lights on village streets. By 1896, the first long-distance transmission of electricity allowed the Niagara Falls project to provide electricity to Buffalo, New York—some 26 miles away.

By the early twentieth century, hydroelectric power was providing more than 40% of electricity generation in the United States. In 1940, hydropower supplied approximately three-fourths of all the electricity consumed in the West and Pacific Northwest, and still supplied approximately one-third of the total U.S. electricity supply. Although hydroelectricity’s share of total electricity generation has since fallen to approximately 10% in the United States, hydroelectricity provides almost one-fifth of the total electricity generation in the world.

See also: Hydroelectric Energy, Hydroelectricity Generation, Hydroelectric Power.

Hydroelectric Energy

Hydroelectric energy, also called hydroelectric power or hydroelectricity, is a form of energy that harnesses the power of water in motion – such as water flowing over a waterfall – to generate electricity. People have used this force for millennia. Over two thousand years ago, people in Greece used flowing water to turn the wheel of their mill to ground wheat into flour.

Since hydroelectric energy is produced by the force of flowing or falling water. The capacity to produce this energy is dependent on both the available flow and the height from which it falls. Building up behind a high dam, water accumulates potential energy. This is transformed into mechanical energy when the water rushes down the sluice and strikes the rotary blades of turbine. The rotation of the turbine spins electromagnets which generate current in stationary coils of wire. Finally, the current is put through a transformer where the voltage is increased for long distance transmission over power lines.

Most hydroelectric power plants have a reservoir of water, a gate or valve to control how much water flows out of the reservoir, and an outlet or place where the water ends up after flowing downward. Water gains potential energy just before it spills over the top of a dam or flows down a hill. The potential energy is converted into kinetic energy as water flows downhill. The water can be used to turn the blades of a turbine to generate electricity, which is distributed to the users.

There are three different types of hydroelectric energy plants, the most common being an impoundment facility. In an impoundment facility, a dam is used to control the flow of water stored in a pool or reservoir. When more energy is needed, water is released from the dam. Once water is released, gravity takes over and the water flows downward through a turbine. As the blades of the turbine spin and power a generator.

Another type of hydroelectric energy plant is a diversion facility. This type of plant is unique because it does not use a dam. Instead, it uses a series of canals to channel flowing river water toward the generator-powering turbines.

The third type of plant is called a pumped-storage facility. This plant collects the energy produced from solar, wind, and nuclear power and stores it for future use. The plant stores energy by pumping water uphill from a pool at a lower elevation to a reservoir located at a higher elevation. When there is high demand for electricity, water located in the higher pool is released. As this water flows back down to the lower reservoir, it turns a turbine to generate more electricity.

In the process of electricity generation, the moving water pushes the turbine blades which turns the rotor, the moving part of the electric generator. When coils of wire on the rotor sweep past the stationary coil of the generator (the stator), electricity is produced. Thus, a hydraulic turbine converts the energy of flowing water into mechanical energy after which a hydroelectric generator converts this mechanical energy into electricity. The operation of a generator is based on the principles discovered by Faraday. He found that when a magnet is moved past a conductor, it causes electricity to flow. In a large generator, electromagnets are made by circulating direct current through loops of wire wound around stacks of magnetic steel laminations (field poles) which are mounted on the perimeter of the rotor. The rotor is attached to the turbine shaft, and rotates at a fixed speed. When the rotor turns, it causes the field poles (the electromagnets) to move past the conductors mounted in the stator. This, in turn, causes electricity to flow and a voltage to develop at the generator output terminals.

Hydroelectric energy is the most commonly-used renewable source of electricity. China is the largest producer of hydroelectricity. Other top producers of hydropower around the world include the United States, Brazil, Canada, India, and Russia. Approximately 71% of all of the renewable electricity generated on Earth is from hydropower.

Pumped storage is a method of keeping water in reserve for peak period power demands by pumping water that has already flowed through the turbines back up a storage pool above the power plant at a time when customer demand for energy is low, such as during the middle of the night. The water is then allowed to flow back through the turbine-generators at times when demand is high and a heavy load is placed on the system. The reservoir acts much like a battery, storing power in the form of water when demands are low and producing maximum power during daily and seasonal peak periods. An advantage of pumped storage is that hydroelectric generating units are able to start up quickly and make rapid adjustments in output. They operate efficiently when used for one hour or several hours. Because pumped storage reservoirs are relatively small, construction costs are generally low compared with conventional hydropower facilities.

As a form of renewable energy, hydropower does not pollute the water or the air. However, hydropower facilities can have large environmental impacts by changing the environment and affecting land use, homes, and natural habitats in the dam area. Most hydroelectric power plants have a dam and a reservoir. These structures may obstruct fish migration and affect their populations. Operating a hydroelectric power plant may also change the water temperature and the flow of the river. These changes may harm native plants and animals in the river and on land. Reservoirs may cover homes, important natural areas, agricultural land, and archaeological sites. So, building dams can require relocating people. Methane, a strong greenhouse gas, may also form in some reservoirs and be emitted to the atmosphere.

Considerable efforts have been made to reduce environmental problems associated with hydropower operations, such as providing safe fish passage and improved water quality as well as efforts to ensure the safety of dams. Yet, many unanswered questions remain related to the best method maintain the economic viability of hydropower in the face of increased demands to protect fish and other environmental resources.

There are many benefits for using hydro resources to produce electricity. First, hydropower is a renewable resource; oil, natural gas, and coal reserves may be depleted over time. Second, hydro resources are indigenous. A country that has developed its hydroelectric resources does not have to depend on other nations for its electricity; hydroelectricity secures a country's access to energy supplies. Third, hydroelectricity is environmentally friendly. It does not emit greenhouse gases, and hydroelectric dams can be used to control floods, divert water for irrigation purposes, and improve navigation on a river.

There are, however, disadvantages to developing hydroelectric power. Hydroelectric dams typically require a great deal of land resources. In conventional hydroelectric projects, a dam typically is built to create a reservoir that will hold the large amounts of water needed to produce power. Further, constructing a hydroelectric dam may harm the ecosystem and affect the population surrounding a hydro project. Environmentalists often are concerned related to the adverse impact of disrupting the flow of a river for fish populations and other animal and plant species. People often must be relocated so that a dam's reservoir may be created. Large-scale dams cause the greatest environmental changes and can be very controversial because of a requirement to relocate people so that a reservoir can be built to serve the dam.

Another potential problem for hydroelectricity is the possibility of electricity supply disruptions. A severe drought can mean that there will not be enough water to operate a hydroelectric facility. Communities with high dependence on the hydroelectric resources may find themselves struggling with electricity shortages in the form of brown-outs and black-outs.

This article begins with a description of how hydroelectricity works, from the beginning of the hydrological cycle to the point at which electricity is transmitted to homes and businesses. The history of the dam is outlined and how dams evolved from structures used for providing a fresh water supply to irrigation and finally to providing electricity. The history of hydropower is considered and the different hydroelectric systems (i.e., conventional, run-of-river, and pumped storage hydroelectricity) currently in use are discussed.

See also: Hydroelectric Energy.

Hydroelectric Power

Hydroelectric power is a widely used renewable source of energy. The idea behind hydroelectric power is conceptually simple. At a geographically and technologically appropriate location along the path of a river, a dam is built creating a huge reservoir lake on the high side of the dam. As reservoir water pours over the dam because of gravity, it turns a turbine which then drives an electric generator, producing electricity.

Hydroelectric power has many attractive advantages such as (i) there are no carbon dioxide emissions or emissions of other serious pollutants during the production of electricity, (ii) large amounts of power are generated in a hydroelectric plant, comparable to that in a coal or nuclear plant, (iii) the conversion efficiency of fluid kinetic energy to electricity is high since no thermal steam cycle is involved, (iv) except in rare cases of extended drought, the power is available continuously for base load electricity, (v) the cost of electricity is low, typically comparable to that of coal plants, and (vi) the fuel reserves are effectively infinite.

Hydroelectric power is clearly a renewable energy source, but there are two disadvantages to hydroelectric power: (i) most of the suitable rivers already have dams and, therefore, expansion of hydroelectric power is difficult since there are few, if any, unutilized technologically attractive sites available, and (ii) although not a major problem for early dams, environmental issues will have a much larger impact on any future hydroelectric plants. The main issue is the large amount of land that is flooded to form the reservoir lake. Often this, land could be used for agricultural or recreational purposes, so there is a tradeoff that must be evaluated before changing its use to electricity production.

As one part of the production of hydroelectric power, dams are placed on a river or other medium-sized body of water to create a reservoir. This reservoir releases water through a turbine, which is spun by the water and powers a generator. Dams and similar constructs also have a variant known as a pumped storage plant, which uses pumps (consuming energy) to move water from a lower reservoir/water source to a higher one, which can then flow back through the turbines to reproduce the energy. As the name suggests, this method is a way for hydroelectric power sources to store energy until it is needed. Dams have been shown to be particularly harmful to their surrounding ecosystem, however, causing shifts in sediment depositories, flooding surrounding land, and killing some of the wildlife that travels through them.

Hydroelectric Power Generation

Hydroelectricity depends on the availability of water, which is provided in the form of rain or melting snow, which fills the reservoirs that fuel the hydroelectric plant. Most of this water comes from oceans, but rivers and lakes and other, smaller bodies of water also contribute. The heat of the sun causes the water from these sources to evaporate (that is, to change the water from its liquid state into a gaseous one). The water remains in the air as an invisible vapor until it condenses and changes first into clouds and eventually into rain. Condensation is the opposite of evaporation. It occurs when the water vapor changes from its gaseous state back into its liquid state.

Condensation occurs when air temperatures cool. The cooling occurs in one of two ways. Either the air vapor cools as it rises and expands or as it comes into contact with a cool object such as a cold landmass or an ice-covered area.

Air rises for several reasons. It can be forced up as it encounters a cooler, denser body of air, or when it meets mountains or other raised land masses. It can rise as it meets a very warm surface, like a desert, and become more buoyant than the surrounding air. Air also can be forced to rise by storms—during tornadoes, particles of air circling to the center of a cyclone collide and are forced up. When the water vapor collides with a cold object, it can become fog, dew, or frost as it condenses. The vapor cools as it rises into the atmosphere and condenses to form clouds and, sometimes, rain.

In order for rain to form, there must be particles in the air (i.e., dust or salt) around which the raindrop can form and which are at temperatures above freezing. When the particles are cooled to temperatures below the freezing point, water condenses around them in layers. The particles grow heavy enough that they eventually fall through the clouds in the form of raindrops or—if the air temperature is below the freezing point, all the way to the ground — as snow, sleet, or hail.

Much of the rain that reaches the ground runs off the surface of the land and flows into streams, rivers, ponds, and lakes. Small streams lead to bigger ones, then to rivers, and eventually back to the oceans where the evaporation process begins all over again. Although water continuously changes from solid to liquid to gas, the amount of water on the earth remains the same, and currently, there is as much water as there was hundreds of millions of years ago.

This water cycle – the process of moving water from oceans to streams and back again – is essential to the generation of hydroelectricity. Moving water can be used to perform work and, in particular, hydroelectric power plants employ water to produce electricity. The combination of abundant rainfall and the right geographical conditions is essential for hydroelectric generation.

Hydroelectric power is generated by flowing water driving a turbine connected to an electric generator. The two basic types of hydroelectric systems are those based on falling water and those based on natural river current, both of which rely on gravitational energy. Gravitational forces pull the water down either from a height or through the natural current of a river. The gravitational energy is converted to kinetic energy. Some of this kinetic energy is converted to mechanical (or rotational) energy by propelling turbine blades that activate a generator and create electricity as they spin.

The amount of energy created by a hydroelectric project depends largely upon two factors: the pressure of the water acting on the turbine and the volume of water available. Water that falls 1,000 feet generates approximately twice as much electric power as the same volume of water falling only 500 feet. In addition, if the amount of water available doubles, so does the amount of energy.

The falling water hydrosystem is comprised of a dam, a reservoir, and a power generating unit. The dam is constructed so that a reservoir is created within which water accumulates and may be stored until it is needed. Water is released as required to meet electricity demands of customers. At the bottom of the dam wall is the water intake. The water intake controls when and how much water is moved into a steel container (the penstock). Gravity causes the water to fall through the penstock. This pipe delivers the running water to a turbine – a propeller-like machine with blades like a large fan. The water pushes against the turbine blades, and the blades turn. Because the turbine is connected to an electric generator, as the turbine gains speed, it powers the generator and electricity is produced. The largest falling water facility in the United States is the Grand Coulee hydroelectric project on the Columbia River, in Washington State. Indeed, the largest power production facilities in North America are found at the Grand Coulee Dam project where an average 21 billion kilowatt-hours of electricity are produced each year.

The second type of hydroelectric plant is called a run-of-the-river system. In this case, the force of the river current applies pressure to the turbine blades to produce electricity. Run-of-the-river systems do not usually have reservoirs and cannot store substantial quantities of water. As a result, power production from this type of system depends on the river flow—the electricity supply is highly dependent upon seasonal fluctuations in output. Run-of-river projects are most successful when there are large flows in flat rivers or when a high natural geological drop is present, and when the required electricity output is below the maximum potential of the site.

Hydropower systems, as in all electricity-producing systems, require a generator to create the electricity. An electric generator is a device that converts mechanical energy into electric energy. The process is based on the relationship between magnetism and electricity. When a wire or any other electrically conductive material moves across a magnetic field, an electric current occurs in the wire. In a power plant, a strong electromagnet, called a rotor, is attached to the end of a shaft. The shaft is used to spin the rotor inside a cylindrical iron shell with slots—called a stator. Conducting wires are wound through the slots of the stator. When the rotor spins at a high rate of speed, an electric current flows through the conducting wires.

In a hydroelectric system, flowing water is used to propel a turbine that spins the shaft connected to the generator and creates the electric current. The kinetic energy of the moving water is changed into rotational energy and thereby

causes the turbine blades to rotate. The turbine is attached to an electric generator, and the rotational energy of the turbine is then converted to electric energy. The electricity then leaves the generator and is carried to the transformers where the electricity can travel through electric power lines and is supplied to residential, commercial, and industrial consumers. After the water has fallen through the turbine, it continues to flow downriver and to the ocean where the water cycle begins all over again.

Pumped storage is an extended version of the falling water hydroelectric system. In a pumped storage system, two water sources are required—a reservoir located at the top of the dam structure and another water source at the bottom. Water released at one level is turned into kinetic energy by its discharge through high-pressure shafts that direct the downflow through the turbines connected to the generator. The water flows through the hydroelectric generating system and is collected in a lower reservoir. The water is pumped back to the upper reservoir once the initial generation process is complete. Generally, this is done using reversible turbines—that is, turbines that can operate when the direction of spinning is reversed. The pump motors are powered by conventional electricity from the national grid. The pumping process usually occurs overnight when electricity demand is at its lowest. Although the pumped storage sites are not net energy producers—pumped storage sites use more energy pumping the water up to the higher reservoir than is recovered when it is released—they are still a valuable addition to electricity supply systems. They offer a valuable reserve of electricity when consumer demand rises unexpectedly or under exceptional weather conditions. Pumped storage systems are normally used as “peaking” units.

See also: Hydroelectric Dams, Hydroelectric Energy, Hydroelectric Power Turbine.

Hydroelectric Power – Turbines

Hydropower plants capture the energy of falling water to generate electricity. A turbine converts the kinetic energy of falling water into mechanical energy. Then, a generator converts the mechanical energy from the turbine into electrical energy.

While there are only two types of turbines – the impulse turbine and the reaction turbine – there are many variations. The specific type of turbine to be used in a powerplant is not selected until all operational studies and cost estimates are complete, and the selection of the turbine depends largely on the site conditions.

An impulse turbine is a horizontal or vertical wheel that uses the kinetic energy of water striking its buckets or blades to cause rotation. The wheel is covered by a housing, and the buckets or blades are shaped so they turn the flow of water approximately 170 degrees inside the housing. After turning the blades or buckets, the water falls to the bottom of the wheel housing and flows out.

A reaction turbine is a horizontal or vertical wheel that operates with the wheel completely submerged, a feature which reduces turbulence. In the reaction turbine, water at a central point is under pressure and escapes from the ends of the blades, causing rotation.

See also: Mechanical Energy, Turbine.

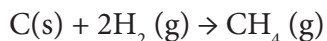
Hydrogasification

Another option for conversion of biomass to useable products is the hydrogasification concept which, although not yet attempted on a commercial scale with biomass, has been used with coal.

Direct addition of hydrogen to coal under high pressure forms methane. This reaction is called hydrogasification that may be written as:



Or



This reaction is exothermic and is thermodynamically favored at low temperatures ($T < 670^{\circ}\text{C}$, $< 1,240^{\circ}\text{F}$), unlike both steam and carbon dioxide gasification reactions. However, at low temperatures, the reaction rate is inevitably too slow. Therefore, high temperature is always required for kinetic reasons, which in turn requires high pressure that is also preferred from equilibrium considerations. This reaction can be catalyzed by potassium carbonate (K_2CO_3), nickel, iron chlorides, and iron sulfate. However, use of catalyst in coal gasification renders somewhat serious economic constraints due to the low raw material value as well as difficulty in recovering and reusing the catalyst. Therefore, catalytic coal gasification has not been practiced much.

See also: Gasification, Gasification of Biomass.

Hydrogen

Hydrogen, as atomic hydrogen, is the most abundant chemical element in the universe, making up 75% w/w normal matter and more than 90% by number of atoms.

Hydrogen (H_2) is a promising energy carrier of the future: It can be derived from a variety of energy sources and used in fuel cells with high efficiency. Hydrogen is a completely clean burning fuel – the product is water (H_2O), and there are no oxides of sulfur or carbon that can cause environmental pollution. The major issue with this form of alternative energy is that it is mostly derived from the use of natural gas and fossil fuels. As such, it could be argued that the emissions created to extract it counteract the benefits of its use. The process of electrolysis, which is essential for the splitting of water into hydrogen and oxygen, makes this less of an issue. However, electrolysis still ranks below the previously mentioned methods for obtaining hydrogen, though research continues to make it more efficient and cost-effective.

Like electricity, hydrogen is an energy carrier (not an energy source), meaning it can store and deliver energy in an easily usable form. Although abundant on earth as an element, hydrogen combines readily with other elements and is almost always found as part of some other substance, such as water (H_2O), or hydrocarbons like natural gas (which consists primarily of methane, CH_4). Hydrogen is also found in biomass, which includes all plants and animals.

Despite its simplicity and abundance, hydrogen does not occur naturally as a gas on the Earth – it is always combined with other elements in the form of naturally-occurring materials. Hydrogen is also found in many organic compounds, notably natural gas, crude oil, heavy crude oil, extra heavy crude oil, and tar sand bitumen which are sources for the currently-used liquid fuels.

The most common industrial methods for producing hydrogen include steam reformation of natural gas, coal gasification, and splitting water with electricity typically generated from fossil fuels. Hydrogen can be separated from hydrocarbon derivatives through the application of heat – a process known as *reforming*. Currently, most hydrogen is made this way from natural gas (steam-methane reforming). An electrical current can also be used to separate water into its components of oxygen and hydrogen (electrolysis), and various species of algae and bacteria, using sunlight as their energy source, even give off hydrogen under certain conditions. Typically, the hydrogen-producing processes are energy-intensive industrial processes that release carbon dioxide and other greenhouse gases and pollutants as by-products. Some microorganisms produce hydrogen naturally, and biotechnologies based on these microbial systems could lead to the development of clean, renewable sources of hydrogen.

The environmental and health benefits are also seen at the source of hydrogen production if derived from low- or zero-emission sources, such as solar, wind, and nuclear energy and fossil fuels with advanced emission controls and carbon sequestration. Because the transportation sector accounts for approximately one-third of carbon dioxide emissions, using these sources to produce hydrogen for transportation can cut greenhouse gas emissions.

The energy content of hydrogen (by volume) is low which makes storing hydrogen a challenge because it requires high pressures, low temperatures, or chemical processes to be stored compactly. Overcoming this challenge is important for light-duty vehicles because they often have limited size and weight capacity for fuel storage.

Typically, the storage capacity for hydrogen in light-duty vehicles should enable a driving range of more than 300 miles to meet consumer needs. Because hydrogen has a lower volumetric energy density than that of gasoline, storing this much hydrogen on a vehicle currently requires a larger tank at higher pressure than other gaseous fuels.

The hydrogen-energy based economy is a proposed system of delivering energy using hydrogen. The advocates promote hydrogen as a potential fuel for motive power (including cars and boats), the energy needs of buildings, and

portable electronics. Free hydrogen does not occur naturally in quantity, but can be generated by steam reforming of hydrocarbon derivatives, electrolysis of water, and a variety of other methods.

In the future, hydrogen could also join electricity as an important energy carrier. An energy carrier moves and delivers energy in a usable form to consumers. Renewable energy sources, such as the sun and wind, cannot produce energy all the time. But they could, for example, produce electric energy and hydrogen, which can be stored until it is needed. Hydrogen can also be transported (like electricity) to locations where it is needed.

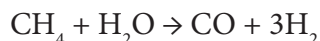
Public awareness of clean burning and energy-efficient hydrogen has propelled unprecedented interest in hydrogen technology and fuel cell research and development. Many experts in the world predict the future as *hydrogen economy*. For the hydrogen economy to be fully arriving, a long list of technological advances must be accomplished, which include technologies for inexpensive generation, safe distribution and storage, safe and efficient materials for hydrogen handling, hydrogen internal combustion engine, hydrogen fuel cells, and loss prevention.

See also: Biohydrogen, Biological Hydrogen Production, Hydrogen Energy, Hydrogen Production.

Hydrogen Economy

Hydrogen is the most abundant element in the universe. It can combine with oxygen to form water, H_2O . This process releases energy, so hydrogen can be used as a fuel. However, natural free hydrogen (hydrogen not already bound up in water or some other molecule) is rare on Earth, so if large quantities are desired, they must be manufactured. This can be done either by reforming methane (CH_4), or by using electricity or catalysts to split water (H_2O) into molecular hydrogen (H_2) and molecular oxygen (O_2), respectively. Hydrogen can be combined with oxygen in a fuel cell, which produces electricity, or in a flame or explosion, which produces heat. In either case, the only chemical byproduct of the reaction is water.

Free hydrogen is found only in trace amounts in nature, so cannot be extracted as a primary chemical fuel. It is therefore considered not an energy source but an energy carrier, a way of moving energy from a primary source to an end-user, much like electricity. Approximately 40 million tons of hydrogen are manufactured each year from natural gas (methane) using a method called the Haber process. This process—named after its discoverer, German chemist Fritz Haber (1868-1934)—exploits the fact that at high temperatures, methane (CH_4 , where C stands for carbon) combines with water in the form of steam to release hydrogen and carbon monoxide (CO). In chemical notation, the reaction is written as follows:



Energy is lost in this reaction—that is, less energy is obtained by burning the hydrogen than could have been obtained by burning the methane from which it was made. Specifically, 15% of the energy in the methane is lost steam reformation. This energy cost may be worthwhile when there is a task that hydrogen can be used for that methane cannot, or if some other value is obtained. For example, more useful energy can be extracted from a given amount of hydrogen in a fuel cell than by burning it explosively with oxygen, as is done in the cylinders of a standard engine. In fact, by reforming methane into hydrogen and then combining the hydrogen with oxygen in a fuel cell, more energy can be extracted from the original methane than by burning it directly, despite the energy lost in the conversion.

Hydrogen is ultimately no cleaner than the energy sources used to produce it. Carbon monoxide is created during the extraction of hydrogen from methane, which, if released into the atmosphere eventually becomes carbon dioxide. However, it is possible to capture this carbon in the large facilities where hydrogen is produced and inject it deep underground to prevent it from causing climate change. Alternatively, there are industrial processes that capture the carbon as a black powder that can be sold as a useful product (carbon black) or sequestered from the atmosphere with relative ease.

Natural gas (which is mostly methane, and is the source of the methane used to manufacture hydrogen) has the advantage of being fairly cheap. There is a well-established supply system for it. However, natural gas has the disadvantage that it is a fossil fuel and will someday be all used up. It is also, like petroleum, often obtained from politically unstable parts of the world. It must be chilled to low temperatures (-160°C , -260°F) and is transported around the

world in gigantic tankers, each one carrying up to 30 million gallons (114 million liters) of super-cold liquid gas that contains as much energy as a small nuclear weapon.

A more attractive way to produce hydrogen than steam reformation of methane, in many ways, is the production of hydrogen by electrolysis using electricity derived from truly inexhaustible resources such as wind power and solar cells. An economy based on electricity from the wind and sunlight, which would use hydrogen wherever a portable liquid fuel was needed, could in theory continue for many millions of years—as long as the sun continues to shine. Such a system might even be affordable.

Despite the many desirable aspects of a global hydrogen economy, transition to a hydrogen economy may be difficult for a number of reasons. Almost every aspect of the possible hydrogen economy is fiercely debated among experts. Some of the issues raised by critics of the concept, along with some of the counterpoints mentioned by its defenders, are as follows: (i) hydrogen is dangerous, and (ii) hydrogen is difficult to handle.

In the first issue (i.e., hydrogen is dangerous), the accident relating to the burning of the airship Hindenburg on May 6, 1937, in Manchester Township, New Jersey is often cited in this respect. Images of the burning hydrogen-filled Hindenburg are often recalled as proof of the dangers of hydrogen. Conversely, gasoline and the other liquid fuels, on which are relied upon for most transportation, are also dangerous and explosive, both as liquids and vapors. In relation to the second issue (i.e., hydrogen is difficult to handle), the hydrogen atom is the smallest and lightest of all atoms, and the hydrogen molecule is the smallest and lightest of all molecules. A given volume of hydrogen contains only 30% as much energy as the same volume of natural gas at the same temperature and pressure; at 2,500 psi, a given volume of hydrogen contains only 6% as much energy as an equal volume of gasoline leading to the concept that hydrogen is therefore bulky and must be transported under pressure, making it difficult to fit enough hydrogen compactly into a vehicle to give it the range of a gasoline-burning conventional or hybrid car.

In the modern world, these aspects of hydrogen behavior require caution but sufficient control are in place to minimize these potential dangers.

See also: Fuel Cell, Hydrogen, Hydrogen Fuel.

Hydrogen – Environmental Impact

Much of the impact of adopting hydrogen as an energy source would be positive for the environment. The use of hydrogen would likely come with a reduction of the use of fossil fuels as energy sources. With this reduction would perhaps come a reduction in global warming because fossil fuel use is believed to be an important contributor to global warming.

However, the production of hydrogen can potentially affect the environment in a negative way. Depending on the production method, carbon dioxide and other negative emissions can enter the atmosphere while hydrogen is being made. This issue can be addressed by catching and storing the carbon dioxide, but even this storage can potentially affect the environment. However, if environmentally friendly, renewable resources such as solar or wind are used to power the means of producing hydrogen, the negative impact can be eliminated.

Another issue is that if hydrogen becomes widely used, it could leak into the atmosphere. If the amount is significant enough, this hydrogen could change the percentage of hydrogen present in Earth's atmosphere. Some scientists believe that this could have a profound effect on the atmosphere, including increasing the size of the hole in the ozone layer. More hydrogen in the atmosphere could also lead to more high altitude clouds and increase the number of soil microbes that rely on hydrogen as their primary nutrient. The soil microbe increase could change the ecology of the Earth. However, there are soil micro-organisms that consume hydrogen as well, and they might be able to balance these problems out. The outcome of putting more hydrogen in the atmosphere is uncertain.

A final environmental question is what to do with the water or water vapor that would be produced by cars using hydrogen fuel cells. Since such water is pure, it will freeze in temperatures below 0°C (32°F).

Hydrogen Fuel

Hydrogen fuel is a zero-emission fuel, which uses electrochemical cells, or combustion in internal engines to power vehicles and electric devices. It is also used in the propulsion of spacecraft and can potentially be mass-produced and

commercialized for passenger vehicles and aircraft. It is a completely clean burning fuel in that its only by-product is water.

As the first element on the Periodic Table of the elements, hydrogen is the lightest element on earth. Since hydrogen gas is so light, it rises in the atmosphere and is therefore rarely found in its pure form (H_2). In a flame of pure hydrogen gas, burning in air, the hydrogen (H_2) reacts with oxygen (O_2) to form water (H_2O) and releases heat. Other than water, hydrogen combustion may yield small amounts of nitrogen oxides.



Pure hydrogen does not occur naturally, and the process takes a substantial amount of energy to manufacture hydrogen. There are different ways to manufacture it, such as, electrolysis and steam-methane reforming process. Once manufactured, this energy carrier can be delivered to fuel cells and generate electricity and heat, or burned to run a combustion engine. Hydrogen fuel can provide motive power for cars, boats, and airplanes, portable fuel cell applications, or stationary fuel cell applications, which can power an electric motor. In each case, hydrogen is combined with oxygen to form water.

Because the process requires a high-energy input, commercial hydrogen is very inefficient. Use of a biological vector as a means to split water, and therefore produce hydrogen gas, would allow for the only energy input to be solar radiation. Biological vectors can include bacteria or more commonly algae. This process is known as biological hydrogen production. It requires the use of single-celled organisms to create hydrogen gas through fermentation. Without the presence of oxygen, also known as an anaerobic environment, regular cellular respiration cannot take place and a process known as fermentation takes over.

Hydrogen – Production

Hydrogen can be produced from diverse domestic resources with the potential for near-zero greenhouse gas emissions. Once produced, hydrogen generates electrical power in a fuel cell, emitting only water vapor and warm air. It holds promise for growth in both the stationary and transportation energy sectors.

Hydrogen can be produced from resources like natural gas, coal, solar energy, wind, and biomass. When used to power highly efficient fuel cell electric vehicles, hydrogen holds the promise of helping conserve petroleum and diversifying the options for energy transportation.

Natural gas is the most common feedstock for hydrogen production since it meets all the requirements for reformer feedstock. Natural gas typically contains more than 90% methane and ethane with only a few percent of propane and higher boiling hydrocarbon derivatives. Natural gas contains traces of carbon dioxide with some nitrogen and other impurities. Purification of natural gas, before reforming, is usually relatively straightforward. Traces of sulfur must be removed to avoid poisoning the reformer catalyst; zinc oxide treatment in combination with hydrogenation is usually adequate.

Low-boiling refinery gas, containing a substantial amount of hydrogen, can be an attractive steam reformer feedstock since it is produced as a by-product. Processing of refinery gas will depend on its composition, particularly the levels of olefins and of propane and heavier hydrocarbon derivatives. Olefin derivatives, that can cause problems by forming coke in the reformer, are converted to saturated compounds in the hydrogenation unit. Higher boiling hydrocarbon derivatives in refinery gas can also form coke, either on the primary reformer catalyst or in the pre-heater. If there is more than a few percent of C_3 and higher compounds, a promoted reformer catalyst should be considered, in order to avoid carbon deposits.

Refinery gas from different sources varies in suitability as hydrogen plant feed. Catalytic reformer off-gas for example, is saturated, low in sulfur, and often has high hydrogen content. The process gases from a coking unit or from a fluid catalytic cracking unit are much less desirable because of the content of unsaturated constituents. In addition to olefins, these gases contain substantial amounts of sulfur that must be removed before the gas is used as

feedstock. These gases are also generally unsuitable for direct hydrogen recovery since the hydrogen content is usually too low. Hydrotreater off-gas lies in the middle of the range. It is saturated, so it is readily used as hydrogen plant feed. Content of hydrogen and higher-boiling hydrocarbon derivatives depends to a large extent on the upstream pressure. Sulfur removal will generally be required.

Under certain conditions, green algae and cyanobacteria can use water-splitting photosynthetic processes to generate molecular hydrogen (H_2) rather than fix carbon, the normal function of oxygenic photosynthesis.

Bidirectional hydrogenases in these organisms use electrons from the photosynthetic electron-transport chain to reduce protons to yield H_2 . Biophotolysis holds potential for the scale of hydrogen production necessary to meet future energy demand. This approach to hydrogen production is promising because the source of electrons or reducing power required to generate hydrogen is water – a clean, renewable, carbon-free substrate available in virtually inexhaustible quantities.

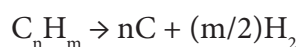
Another advantage of biophotolysis is the more efficient conversion of solar energy to hydrogen. Reengineering microbial systems for the direct production of hydrogen from water eliminates inefficiencies associated with carbon fixation and biomass formation. Theoretically, the maximal energetic efficiency for direct biophotolysis is approximately 40% compared with a maximum of approximately 1% for hydrogen production from biomass.

Each process for the production of hydrogen-producing method has advantages and disadvantages. Electrolysis is considered to be the most environmentally-benign procedure because it produces no by-products that are harmful to the environment. In addition, it has a potentially positive by-product: oxygen which can be captured and used elsewhere. Although the large-scale production of hydrogen by electrolysis is generally an expensive process when electricity is used to create the electric currents, the use of renewable energy sources such as hydroelectric power, hydropower, solar energy or even nuclear power are used to produce the current can lower the cost of the production process. Another source of energy could be obtained through the use of biomass: waste, sewage, and agricultural residue are all endlessly renewable and have little negative effect on the environment.

See also: High Temperature Water Splitting, Hydrogen, Hydrogen Production.

Hydrogen – Production By Pyrolysis

Natural gas is readily available and offers a relatively rich stream of methane with lower amounts of ethane, propane, and butane also present. The thermocatalytic decomposition of natural gas hydrocarbon derivatives offers an alternate method for the production of hydrogen:



If a hydrocarbon fuel such as natural gas (methane) is to be used for hydrogen production by direct decomposition, then the process that is optimized to yield hydrogen production may not be suitable for production of high-quality carbon black by-product intended for the industrial rubber market. Moreover, it appears that the carbon produced from high-temperature (850-950°C; 1,560-1,740°F) direct thermal decomposition of methane is a soot-like material with high tendency for the catalyst deactivation. Thus, if the object of methane decomposition is hydrogen production, the carbon by-product may not be marketable as high-quality carbon black for rubber and tire applications.

The production of hydrogen by direct decomposition of hydrogen sulfide is also a possibility. The process is highly endothermic, and equilibrium yields are poor. At temperatures less than 1,500°C (2,730°F), the thermodynamic equilibrium is unfavorable toward hydrogen formation. However, in the presence of catalysts such as platinum-cobalt (at 1,000°C; 1,830°F), disulfides of molybdenum or tungsten Mo or W at 800°C (1,470°F), or other transition metal sulfides supported on alumina (at 500 to 800°C; 930 to 1,470°F), decomposition of hydrogen sulfide proceeds rapidly. In the temperature range of approximately 800 to 1,500°C (1,470 to 2,730°F), thermolysis of hydrogen sulfide can be treated simply:

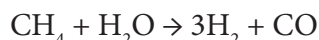


where $x = 2$. Outside this temperature range, multiple equilibria may be present depending on temperature, pressure, and relative abundance of hydrogen and sulfur.

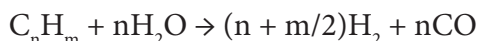
Above approximately 1,000°C (1,830°F), there is a limited advantage to using catalysts since the thermal reaction proceeds to equilibrium very rapidly. The hydrogen yield can be doubled by preferential removal of either H_2 or sulfur from the reaction environment, thereby shifting the equilibrium. The reaction products must be quenched quickly after leaving the reactor to prevent reversible reactions.

Hydrogen Production Chemistry

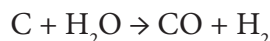
In the steam reforming process, low-boiling hydrocarbon derivatives such as methane are reacted with steam to form hydrogen:



H is the heat of reaction. A more general form of the equation that shows the chemical balance for higher-boiling hydrocarbon derivatives is:



The reaction is typically carried out at approximately 815°C (1,500°F) over a nickel catalyst packed into the tubes of a reforming furnace. The high temperature also causes the hydrocarbon feedstock to undergo a series of cracking reactions, plus the reaction of carbon with steam:



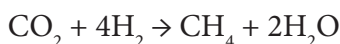
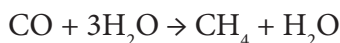
Carbon is produced on the catalyst at the same time that hydrocarbon is reformed to hydrogen and carbon monoxide. With natural gas or similar feedstock, reforming predominates and the carbon can be removed by reaction with steam as fast as it is formed. When higher-boiling feedstocks are used, the carbon is not removed fast enough and builds up thereby requiring catalyst regeneration or replacement. Carbon buildup on the catalyst (when high-boiling feedstocks are employed) can be avoided by addition of alkali compounds, such as potash, to the catalyst thereby encouraging or promoting the carbon-steam reaction.

However, even with an alkali-promoted catalyst, feedstock cracking limits the process to hydrocarbon derivatives with a boiling point less than of 180°C (350°F). Natural gas, propane, butane, and low-boiling naphtha are most suitable. Pre-reforming, a process that uses an adiabatic catalyst bed operating at a lower temperature, can be used as a pretreatment to allow heavier feedstocks to be used with lower potential for carbon deposition (coke formation) on the catalyst.

After reforming, the carbon monoxide in the gas is reacted with steam to form additional hydrogen (the water-gas shift reaction):



This leaves a mixture consisting primarily of hydrogen and carbon monoxide that is removed by conversion to methane:



The critical variables for steam reforming processes are (i) temperature, (ii) pressure, and (iii) the steam/hydrocarbon ratio. Steam reforming is an equilibrium reaction, and conversion of the hydrocarbon feedstock is favored by high temperature, which in turn requires higher fuel use. Because of the volume increase in the reaction, conversion is also favored by low pressure, which conflicts with the need to supply the hydrogen at high pressure. In practice, materials of construction limit temperature and pressure.

On the other hand, and in contrast to reforming, shift conversion is favored by low temperature. The gas from the reformer is reacted over iron oxide catalyst at 315 to 370°C (600 to 700°F) with the lower limit being dictated activity of the catalyst at low temperature.

Hydrogen can also be produced by partial oxidation (POX) of hydrocarbon derivatives in which the hydrocarbon is oxidized in a limited or controlled supply of oxygen:



The shift reaction also occurs, and a mixture of carbon monoxide and carbon dioxide is produced in addition to hydrogen. The catalyst tube materials do not limit the reaction temperatures in partial oxidation processes, and higher temperatures may be used that enhance the conversion of methane to hydrogen. Indeed, much of the design and operation of hydrogen plants involves protecting the reforming catalyst and the catalyst tubes because of the extreme temperatures and the sensitivity of the catalyst. In fact, minor variations in feedstock composition or operating conditions can have significant effects on the life of the catalyst or the reformer itself. This is particularly true of changes in molecular weight of the feed gas, or poor distribution of heat to the catalyst tubes.

Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the lower-boiling feedstocks that are required for steam reforming. Partial oxidation processes were first considered for hydrogen production because of expected shortages of lower-boiling feedstocks and the need to have available a disposal method for higher-boiling, high-sulfur streams such as asphalt or petroleum coke.

Catalytic partial oxidation, also known as auto-thermal reforming, reacts oxygen with a low-boiling feedstock and by passing the resulting hot mixture over a reforming catalyst. The use of a catalyst allows the use of lower temperatures than in non-catalytic partial oxidation and which causes a reduction in oxygen demand.

The feedstock requirements for catalytic partial oxidation processes are similar to the feedstock requirements for steam reforming, and low-boiling hydrocarbon derivatives from refinery gas to naphtha are preferred. The oxygen substitutes for much of the steam in preventing coking and a lower steam/carbon ratio is required. In addition, because a large excess of steam is not required, catalytic partial oxidation produces more carbon monoxide and less hydrogen than steam reforming. Thus, the process is more suited to situations where carbon monoxide is the more desirable product such as, for example, as synthesis gas for chemical feedstocks.

Hydrogen Production Processes

In spite of the use of low-quality hydrogen (that contain up to 40% by volume hydrocarbon gases), a high-purity hydrogen stream (95%-99% by volume hydrogen) is required for hydrodesulfurization, hydrogenation, hydrocracking, and petrochemical processes. Hydrogen, produced as a by-product of refinery processes (principally hydrogen recovery from catalytic reformer product gases), often is not enough to meet the total refinery requirements, necessitating the manufacturing of additional hydrogen or obtaining supply from external sources.

Catalytic reforming remains an important process used to convert low-octane naphtha into high-octane gasoline blending components called reformate. Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, and isomerization taking place simultaneously. Hydrogen, a significant by-product, is separated from reformate for recycling and use in other processes.

A catalytic reformer comprises a reactor section and a product-recovery section. More or less standard is a feed preparation section in which, by combination of hydrotreatment and distillation, the feedstock is prepared to specification. Most processes use platinum as the active catalyst. Sometimes, platinum is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal. There are many different commercial catalytic reforming processes including Platforming, Powerforming, Ultraforming, and Thermoform catalytic reforming. In the platforming process,

the first step is preparation of the naphtha feed to remove impurities from the naphtha and reduce catalyst degradation. The naphtha feedstock is then mixed with hydrogen, vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing a platinum catalyst. The effluent from the last reactor is cooled and sent to a separator to permit removal of the hydrogen-rich gas stream from the top of the separator for recycling. The liquid product from the bottom of the separator is sent to a fractionator called a stabilizer (butanizer), and the bottom product (reformate) is sent to storage, and low-boiling gases butane derivatives pass overhead and are sent to the saturated gas plant.

Some catalytic reformers operate at low pressure (50-200 psi), and others operate at high pressures (up to 1,000 psi). Some catalytic reforming systems continuously regenerate the catalyst in other systems. One reactor at a time is taken off-stream for catalyst regeneration, and some facilities regenerate all of the reactors during turnarounds. Operating procedures should be developed to ensure control of hot spots during start-up. Safe catalyst handling is important, and care must be taken not to break or crush the catalyst when loading the beds, as the small fines will plug up the reformer screens. Precautions against dust when regenerating or replacing catalyst should also be considered, and a water wash should be considered where stabilizer fouling has occurred due to the formation of ammonium chloride and iron salts. Ammonium chloride may form in pretreater exchangers and cause corrosion and fouling. Hydrogen chloride from the hydrogenation of chlorine compounds may form acid or ammonium chloride salt.

Electrolytic processes use electricity to split water into hydrogen and oxygen in a unit called an electrolyzer. Like fuel cells, electrolyzers consist of an anode and a cathode separated by an electrolyte. The electrolyte determines the type of electrolyzer and its operating conditions.

In a polymer electrolyte membrane (PEM) electrolyzer, (i) water at the anode reacts to form oxygen and positively charged hydrogen ions (protons) and electrons that flow through the external circuit, (ii) the hydrogen ions move across the polymer electrolyte membrane to the cathode, and (iii) at the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas.

Alkaline electrolyzers are similar to polymer electrolyte membrane electrolyzers, but instead use an alkaline solution (of sodium or potassium hydroxide) as the electrolyte. Both PEM and alkaline electrolyzers operate at relatively low temperatures on the order of 80 to 100°C (176 to 212°F) and 100 to 250°C (212 to 480°F), respectively. A solid oxide electrolyzer, which has a solid ceramic electrolyte, generates hydrogen in a slightly different way and must operate at a higher temperature (500 to 800°C, 930 to 1,470°F) for the membranes to function properly. Solid oxide electrolyzers can effectively use heat available at these elevated temperatures (from various sources, including nuclear energy) to decrease the amount of electrical energy needed to produce hydrogen from water. In a solid oxide electrolyzer, (i) water at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions, and (iii) the oxygen ions pass through the membrane and react at the anode to form oxygen gas and give up the electrons to the external circuit.

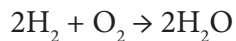
Polymer electrolyte membranes and alkaline electrolyzers can be smaller, appliance-sized equipment, and well suited for distributed hydrogen production. The source of the required electricity (including its cost and efficiency, as well as emissions resulting from electricity generation) must be considered when evaluating the benefits of hydrogen production via electrolysis.

See also: High Temperature Water Splitting.

Hydrogen Properties

Combustion

Combustion of hydrogen with the oxygen in the air. When the bottom cap is removed, allowing air to enter at the bottom, the hydrogen in the container rises out of top and burns as it mixes with the air. Hydrogen gas is highly flammable:



Gas gas liquid

Hydrogen gas forms explosive mixtures with air in concentrations from 4 to 74% v/v and with chlorine at 5 to 95% v/v. The explosive reactions may be triggered by spark, heat, or sunlight. The hydrogen autoignition temperature (the temperature of spontaneous ignition in air, is 500°C (932°F).

Isotopes

Hydrogen has three naturally occurring isotopes, denoted ^1H , ^2H , and ^3H . Other, highly unstable nuclei (^4H to ^7H) have been synthesized in the laboratory but not observed in nature.

The ^1H isotope is the most common hydrogen isotope, with an abundance of more than 99.98%. Because the nuclear of this isotope consists of only a single proton, it is given the descriptive but rarely used formal name *protium*.

The ^2H isotope, the other stable hydrogen isotope, is known as deuterium and contains one proton and one neutron in the nucleus. Deuterium is not radioactive, and does not represent a significant toxicity hazard. Water enriched in molecules that include deuterium instead of normal hydrogen is called heavy water. Deuterium and its compounds are used as a non-radioactive label in chemical experiments and in solvents for ^1H -NMR spectroscopy. Heavy water is used as a neutron moderator and coolant for nuclear reactors. Deuterium is also a potential fuel for commercial nuclear fusion.

The ^3H isotope (known as tritium) contains one proton and two neutrons in the nucleus. It is radioactive, decaying into helium-3 (^3He) through beta-decay, and has a half-life of 12.32 years. Tritium (in small amounts) is produced naturally by the interaction of cosmic rays with atmospheric gases; tritium has also been released during testing of nuclear weapons.

The symbols D and T (instead of ^2H and ^3H) are sometimes used for deuterium and tritium, but the corresponding symbol for protium, P, is already in use for phosphorus and thus is not available for protium.

See also: Nuclear Energy, Nuclear Fission, Nuclear Fusion.

Hydrogen Purification

When the hydrogen content of the refinery gas is greater than 50% by volume, the gas should first be considered for hydrogen recovery, using a membrane or pressure swing adsorption unit. The tail gas or reject gas that will still contain a substantial amount of hydrogen can then be used as steam reformer feedstock. Generally, the feedstock purification process uses three different refinery gas streams to produce hydrogen. First, high-pressure hydrocracker purge gas is purified in a membrane unit that produces hydrogen at medium pressure and is combined with medium pressure off-gas that is first purified in a pressure swing adsorption unit. Finally, low-pressure off-gas is compressed, mixed with reject gases from the membrane and pressure swing adsorption units, and used as steam reformer feed.

Various processes are available to purify the hydrogen stream, but since the product streams are available as a wide variety of composition, flows, and pressures, the best method of purification will vary. And there are several factors that must also be taken into consideration in the selection of a purification method. These are: (i) hydrogen recovery, (ii) product purity, (iii) pressure profile, and (iv) reliability. Cost, an equally important parameter, is not considered here since the emphasis is on the technical aspects of the purification process.

Wet scrubbing systems, particularly amine or potassium carbonate systems, are used for removal of acid gases such as hydrogen sulfide or carbon dioxide. Most systems depend on chemical reaction and can be designed for a wide range of pressures and capacities. They were once widely used to remove carbon dioxide in steam reforming plants, but have generally been replaced by pressure swing adsorption units except where carbon monoxide is to be recovered. Wet scrubbing is still used to remove hydrogen sulfide and carbon dioxide in partial oxidation plants.

Wet scrubbing systems remove only acid gases or high-boiling hydrocarbon derivatives, but they do not methane or other hydrocarbon gases, hence have little influence on product purity. Therefore, wet scrubbing systems are most often used as a pretreatment step, or where a hydrogen-rich stream is to be desulfurized for use as fuel gas.

See also: Gas Cleaning.

Hydrogenation and Hydrolysis Processes

The reduction of carbonyl sulfide, carbon disulfide, sulfur dioxide, and sulfur vapor in Claus tail gas to hydrogen sulfide is necessary when sulfur recovery of 99.9+% is required. Usually, the sulfur recovery level is set by the allowable emissions of sulfur from the tail gas incinerator. In addition, the reduction of carbonyl sulfide is done on raw synthesis gas when the downstream acid gas removal process is unable to remove carbonyl sulfide to a sufficient extent to meet sulfur emissions regulations from combustion of the cleaned fuel gas. These sulfur compounds are reduced to hydrogen sulfide by hydrogenation or by hydrolysis, at a raised temperature, over a catalytic bed.

In these processes, elemental sulfur and sulfur dioxide are reduced mainly via hydrogenation, while carbonyl sulfide and carbon disulfide are mainly hydrolyzed to hydrogen sulfide. Sulfur and sulfur dioxide are virtually completely converted to hydrogen sulfide when an excess of hydrogen is present.

The hydrogen can be supplied from an outside source, can already be in the Claus tail gas, or obtained by partial oxidation of the fuel gas in a furnace. The tail gas is preheated to the reactor temperature by an in-line burner that combusts fuel gas directly into the tail gas. The same burner can also be used to supply the needed hydrogen by partial combustion of the fuel gas.

When oxygen enrichment is used in the Claus plant, there is often sufficient hydrogen in the tail gas to carry out the reduction without an outside hydrogen source. There is usually sufficient water vapor in the Claus tail gas for the hydrolysis reactions.

The SCOT (Shell Claus Off-gas Treating) process was developed in the early 1970s and consists of a combination of a catalytic hydrogenation/hydrolysis step and an amine scrubbing unit. The hydrogenation/hydrolysis of the sulfur compounds in the tail gases from the Claus unit has already been covered above.

The early SCOT units consisted of a hydrogenation/hydrolysis reactor and a conventional amine unit. The Claus tail gas, after being reduced in the reactor, is cooled in a quench column and scrubbed by a Sulfinol solution. The clean tail gas goes to a Claus incinerator, and the acid gas-rich solution is regenerated in a stripping column. The acid gas off the top of the stripper is recycled back to the Claus plant for further conversion of the hydrogen sulfide. The absorber is operated at near atmospheric pressure, and the amine solvent is not highly loaded with acid gases. Because the solution is not highly loaded, unlike high pressure operation, there is no need for an intermediate flash vessel and the loaded solution goes directly to a stripper.

Early SCOT units used diisopropanolamine in the Sulfinol (Sulfinol-D) solution. Methyl diethanolamine-based Sulfinol (Sulfinol-M) was used later to enhance hydrogen sulfide removal and to allow for selective rejection of carbon dioxide in the absorber.

To achieve the lowest possible hydrogen sulfide content in the treated gas, the Super-SCOT configuration was introduced. In this version, the loaded Sulfinol-M solution is regenerated in two stages. The partially stripped solvent goes to the middle of the absorber, while the fully stripped solvent goes to the top of the absorber. The solvent going to the top of the absorber is cooled below that used in the conventional SCOT process.

The SCOT process can be configured in various ways. For example, it can be integrated with the upstream acid gas removal unit if the same solvent is used in both units. Another configuration has been used to cascade the upstream gas cleanup with the SCOT unit. A hydrogen sulfide-lean acid gas from the upstream gas treating unit is sent to a SCOT process with two absorbers. In the first absorber, the hydrogen sulfide-lean acid gas is enriched, while the second absorber treats the Claus tail gas. A common stripper is used for both SCOT absorbers and, in this latter configuration, different solvents could be used in both the upstream and the SCOT units.

See also: Gas Cleaning.

Hydrogen Energy

Hydrogen is the simplest element on earth. An atom of hydrogen has only one proton and one electron. Hydrogen gas is a diatomic molecule—each molecule has two atoms of hydrogen (H_2). At standard temperature and pressure, hydrogen exists as a gas. It is colorless, odorless, tasteless, and lighter (less dense) than air. Like electricity, hydrogen is an energy carrier (not an energy source), meaning it can store and deliver energy in an easily usable form. Although abundant on earth as an element, hydrogen combines readily with other elements and is almost always found as part

of some other substance, such as water (H_2O), or hydrocarbon derivatives like natural gas (which consists primarily of methane, CH_4). Hydrogen is also found in biomass, which includes all plants and animals.

Fuel cells use hydrogen to create electricity, with only heat and water as by-products. When used to power a vehicle, the only output from the tailpipe is water vapor—no greenhouse gas or criteria emissions. To realize the environmental benefits of hydrogen, however, consideration must be given to the full fuel cycle (also called “well-to-wheels”) – from energy source to hydrogen production to end-use. Producing hydrogen from renewable sources or nuclear energy yields virtually zero greenhouse gas emissions. Hydrogen produced from coal, when combined with capture and sequestration of the by-product carbon dioxide, also results in virtually no greenhouse gas emissions.

Thermal processes use the energy in resources including natural gas, coal, or biomass to produce hydrogen. Some “thermochemical” processes use heat combined with closed chemical cycles to produce hydrogen from feedstocks such as water. Thermal processes include (i) natural gas reforming – natural gas reforming natural gas contains methane (CH_4) that can be used to produce hydrogen via thermal processes, (ii) gasification of hydrocarbonaceous feedstocks, (iii) renewable liquid fuel reforming, (iv) high temperature water splitting, and (v) partial oxidation of hydrocarbonaceous feedstocks. Hydrogen can also be produced via steam reforming of fuels including gasoline, propane, and ethanol; however, approximately 95% of the hydrogen produced in the United States is produced by steam-methane reforming, in which high-temperature steam ($700 - 1,000^\circ\text{C}$, $1,830^\circ\text{F}$) is used to produce hydrogen from a methane source such as natural gas. The methane reacts with steam under 45 to 375 psi pressure in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. The carbon monoxide and steam are then reacted using a catalyst to produce carbon dioxide and more hydrogen – the water-gas shift reaction. In the final process step – the pressure-swing adsorption step – carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen.

In the partial oxidation process, the methane and other hydrocarbon derivatives in natural gas are reacted with a limited amount of oxygen (typically from air) that is not enough to completely oxidize the hydrocarbon derivatives to carbon dioxide and water. With less than the stoichiometric amount of oxygen available for the reaction, the reaction products contain primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), again with a relatively small amount of carbon dioxide and other compounds. The product gas is often referred to as synthesis gas (or syngas) from which hydrogen can be separated for use. Unlike steam reforming, which is an endothermic process that requires heat, partial oxidation is an exothermic process that gives off heat. Typically, it is much faster than steam reforming and requires a smaller reactor vessel. As illustrated in the chemical reactions (see sidebar), partial oxidation initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel. As in steam reforming, to maximize the amount of hydrogen produced, partial oxidation usually includes a water-gas shift reaction to generate additional hydrogen from the oxidation of carbon monoxide to carbon dioxide by reaction with water (steam).

Biomass includes crop or forest residues; special crops grown specifically for energy use like switchgrass or willow trees; and organic municipal solid waste. Because biomass resources often consume carbon dioxide in the atmosphere as part of their natural growth processes, producing hydrogen through biomass gasification may release near-zero net greenhouse gases.

Electrolytic processes use electricity to split water into hydrogen and oxygen in a unit called an electrolyzer. Like fuel cells (see page 25), electrolyzers consist of an anode and a cathode separated by an electrolyte. The electrolyte determines the type of electrolyzer and its operating conditions. In a polymer electrolyte membrane (PEM) electrolyzer. Water at the anode reacts to form oxygen and positively charged hydrogen ions (protons) and electrons that flow through the external circuit. The hydrogen ions move across the polymer electrolyte membrane to the cathode. At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas. Alkaline electrolyzers are similar to polymer electrolyte membrane electrolyzers, but instead use an alkaline solution (of sodium or potassium hydroxide) as the electrolyte. Both PEM and alkaline electrolyzers operate at relatively low temperatures – 80 to 100°C (176 to 212°F) and 100 to 250°C (212 to 480°F), respectively.

Electricity can be generated using renewable resources such as wind, solar, geothermal, or hydro-electric power. Hydrogen production via “renewable electrolysis” offers opportunities for synergy with variable power generation. For example, though the cost of wind power has continued to drop, the inherent variability of wind impedes its widespread use. Co-production of hydrogen and electric power could be integrated at a wind farm, allowing flexibility and the ability to shift production to match the availability of resources with the operational needs and market factors of the system.

Biomass resources, when converted to ethanol, bio-oils, or other liquid fuels, can be transported at relatively low cost to the point of use and reformed onsite to produce hydrogen. Reforming renewable liquids is similar to reforming natural gas. The liquid fuel is reacted with steam at high temperatures in the presence of a catalyst to produce a reformat gas composed of mostly hydrogen and carbon monoxide. Reacting the carbon monoxide with steam in a water-gas shift reaction produces additional hydrogen and carbon dioxide.

Since renewable liquids consist of higher molecular weight constituents, they can be somewhat more difficult to reform than the methane in natural gas. Better catalysts will improve hydrogen yields and selectivity. And like natural gas reforming, operation, maintenance, and capital equipment costs must be reduced and the energy efficiency must be improved for the hydrogen produced to be cost-competitive with conventional fuels.

See Also: Fuel Cells, Hydrogen.

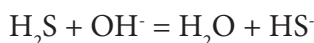
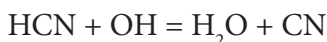
Hydrogen Sulfide

Hydrogen sulfide (Table H-5) is the chemical compound with the formula H_2S . It is a colorless chalcogen hydride gas with the characteristic foul odor of rotten eggs. It is poisonous, corrosive, and flammable.

Table H-5 General properties of hydrogen sulfide.

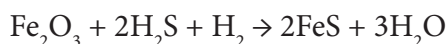
Property	Data
Formula	H_2S
Molar mass	34.1 g/mol
Boiling point	-60°C (-76°F)
Melting point	-85.5°C (-121.9°F)
Soluble in	water and alcohol

The thermal decomposition of biomass feedstocks can produce hydrogen sulfide (as well as hydrogen cyanide) which can be removed by alkaline scrubbing of coal gas by conversion to nonvolatile species:



Each process is reversible (by neutralization), which facilitates recovery of hydrogen cyanide and hydrogen sulfide from the scrubber solutions.

Hydrogen sulfide can be removed from gas streams at relatively high temperatures using solid sorbents. The process (at approximately 540°C ; 1005°F) involves the reaction of hydrogen sulfide with hydrogen in the presence of iron oxide:



Ensuing regeneration of the sorbent is accomplished by high-temperature reaction with oxygen to yield a concentrated stream of sulfur dioxide and regenerated iron oxide.

See also: Gas Cleaning, Hydrogen Sulfide Control, Hydrogen Sulfide Conversion, Hydrogen Sulfide Removal.

Hydrogen Sulfide – Control

The systems for removing hydrogen sulfide that are available to be used for oil shale operations can generally remove at least 98% of this pollutant. Such processes will probably be applied to gas streams from retorting and upgrading

operations. The Beavon Process, Claus Process, IFP Process, SCOT Process, Selexol Process, and Stretford Process are used as examples.

In the Beavon process, the tail gas from a Claus plant is mixed with hot combustion gases and passed through a catalyst where all the sulfur compounds are converted to hydrogen sulfide. The hydrogen sulfide-rich gas is cooled by a slightly alkaline buffer solution and then treated in a Stretford unit. The Beavon process is also adversely affected by high concentrations of carbon dioxide in the feed stream. Its use in oil shale plants would require adaptations similar to those needed for the SCOT process.

The Claus process, which is the oldest and best known method for recovering sulfur from streams that contain both hydrogen sulfide and sulfur dioxide, has several variations. With a feed stream containing only hydrogen sulfide, the required sulfur dioxide is obtained by oxidizing part of the hydrogen sulfide to sulfur dioxide by burning it in air, and then mixing the combustion products with the feed stream. The hydrogen sulfide and sulfur dioxide are then reacted with each other in a series of converters to produce elemental sulfur, which is removed by condensation. The feed stream must have a relatively high concentration of sulfur compounds in order to achieve high conversion efficiency with reasonable equipment size. This process has problems with both maintenance and downtime. Thus backup units are often needed. Problems arise from sulfur condensation in the supply and product pipelines. The tail gas (treated gas) from a Claus plant still contains fairly sizable concentrations of hydrogen sulfide to sulfur dioxide and can be recirculated, mixed with a large volume of stack gas and released, or treated in other systems. In oil shale plants, it is likely that the Claus plant effluent would require further treatment before being released using processes such as the SCOT process, the Beavon process, and the IFP process.

In the SCOT process (Shell Claus Offgas Treating process), the offgas is heated with a reducing gas such as hydrogen, and the mixture is passed through a cobalt-molybdate catalyst bed where all the sulfur compounds are reduced to hydrogen sulfide. The gas is then sent through an absorber where the hydrogen sulfide is dissolved and concentrated. The concentrated hydrogen sulfide is liberated from the absorbing medium by heating and is returned to the Claus plant. The SCOT process is adversely affected by high concentrations of carbon dioxide, and since gaseous emissions from oil shale processing are expected to be rich in carbon dioxide, higher rates of recycling, more complete fuel combustion, and perhaps steam injection to dissolve the carbon dioxide may be necessary.

The IFP process (Institut Français du Pétrole process) uses the same basic reaction as the Claus process except that it takes place in a liquid rather than a gaseous phase. The liquid is a polyalkylene glycol with a 5% concentration of a glycol ester catalyst. Both hydrogen sulfide and sulfur dioxide are very soluble in this liquid, and efficient conversion to sulfur results. The most important operating variable is the hydrogen sulfide/sulfur dioxide, which must be at least 2. The process is flexible and can accommodate wide changes in contaminant concentrations while maintaining constant conversion rates. Also, because the gases can be treated at higher temperatures than in other processes, heat losses are reduced.

The Selexol process is a physical absorption processes in which the hydrogen sulfide is dissolved in a solvent and subsequently recovered. The solvent is recycled. The earliest process, a simple water wash, was inefficient because hydrogen sulfide is not very soluble in water. Modern processes use solvents in which it is more readily dissolved. Absorption processes are usually used for treating high-pressure gases and for reducing the concentrations of hydrogen sulfide and other sulfur compounds to extremely low levels. These processes involve the selective absorption of hydrogen sulfide from gases containing carbon dioxide. This produces a hydrogen sulfide-rich stream that can be processed in a Claus plant. Absorption processes can also remove sulfur compounds, such as carbonyl sulfide, carbon disulfide, mercaptans, and thiophenes, which cannot be processed in a Stretford unit. Because of its low cost and simplicity, the Selexol process is a good candidate for use in oil shale plants.

In the Stretford process, the gas stream is scrubbed in an absorption tower with a solution containing sodium carbonate, sodium metavanadate, and anthraquinone disulfonic acid (ADA). Reduction of the metavanadate with hydrogen sulfide in solution causes sulfur to precipitate. The metavanadate is regenerated by oxidation with the anthraquinone disulfonic acid, and the reduced anthraquinone disulfonic acid is then regenerated by being oxidized in an air stream. The process was originally developed for coal-gas treatment, but it has been used for many other purposes in a number of plants. Any carbonyl sulfide (COS) and carbon disulfide (CS₂) that may also be in the gas stream would not be removed in this process, and their presence would interfere with hydrogen sulfide removal. Therefore, before hydrogen sulfide removal, the gas stream would need to be pretreated to remove these compounds.

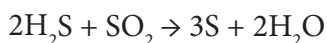
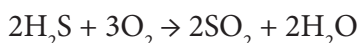
See also: Beavon Process, Claus Process, Gas Cleaning, Gas Processing, Gas Treating, Hydrogen Sulfide, Hydrogen Sulfide Conversion, Hydrogen Sulfide Removal, SCOT Process.

Hydrogen Sulfide Conversion

The disposition of hydrogen sulfide is an issue with many gas processing operations. Burning hydrogen sulfide as a fuel gas component or as a flare gas component is precluded by safety and environmental considerations since one of the combustion products is the highly toxic sulfur dioxide (SO_2), which is also toxic.

As described above, hydrogen sulfide is typically removed from gas streams through an olamine process after which application of heat regenerates the olamine and forms an acid gas stream (also called the tail gas stream). Following from this, the acid gas stream is treated to convert the hydrogen sulfide to elemental sulfur and water. The conversion process utilized in most modern refineries is the Claus process, or a variant thereof.

The Claus process involves combustion of approximately one-third of the hydrogen sulfide to sulfur dioxide and then reaction of the sulfur dioxide with the remaining hydrogen sulfide in the presence of a fixed bed of activated alumina, cobalt molybdenum catalyst resulting in the formation of elemental sulfur:



Different process flow configurations are in use to achieve the correct hydrogen sulfide/sulfur dioxide ratio in the conversion reactors.

Overall, conversion of 96 to 97% of the hydrogen sulfide to elemental sulfur is achievable in a Claus process. If this is insufficient to meet air quality regulations, a Claus process tail gas treater is utilized to remove essentially the entire remaining hydrogen sulfide in the tail gas from the Claus unit. The tail gas treater may employ a proprietary solution to absorb the hydrogen sulfide followed by conversion to elemental sulfur.

The SCOT (Shell Claus Off-gas Treating) unit is also used to treat tail gas and uses a hydrotreating reactor followed by amine scrubbing to recover and recycle sulfur, in the form of hydrogen, to the Claus unit). In the process, tail gas (containing hydrogen sulfide and sulfur dioxide) is contacted with hydrogen and reduced in a hydrotreating reactor to form hydrogen sulfide and water. The catalyst is typically cobalt/molybdenum on alumina. The gas is then cooled in a water contractor. The hydrogen sulfide-containing gas enters an amine absorber which is typically in a system segregated from the other refinery amine systems. The purpose of segregation is two-fold, and that is (i) the tail gas treater frequently uses a different amine than the rest of the plant, and (ii) the tail gas is frequently cleaner than the refinery fuel gas (in regard to contaminants), and segregation of the systems reduces maintenance requirements for the SCOT unit. Amines chosen for use in the tail gas system tend to be more selective for hydrogen sulfide and are not affected by the high levels of carbon dioxide in the off-gas.

The hydrotreating reactor converts sulfur dioxide in the off-gas to hydrogen sulfide that is then contacted with a Stretford solution (a mixture of a vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide) in a liquid-gas absorber. The hydrogen sulfide reacts stepwise with sodium carbonate and the anthraquinone sulfonic acid to produce elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber.

Other tail gas treating processes include (i) caustic scrubbing, (ii) polyethylene glycol treatment, (iii) Selectox process, and (iv) sulfite/bisulfite tail gas treating.

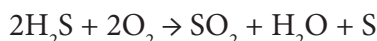
See also: Gas Cleaning, Hydrogen Sulfide, Hydrogen Sulfide Hydrogen Sulfide Removal.

Hydrogen Sulfide Removal

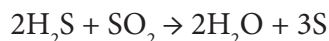
Hydrotreating creates hydrogen sulfide gas that requires disposal. The usual process is a two-stage operation involving (i) the removal of the hydrogen sulfide from the gas stream from the hydrocarbon stream, and (ii) the conversion of the hydrogen sulfide in a gas stream to elemental sulfur.

Removal of the hydrogen sulfide from the hydrocarbon stream can be accomplished by a number of different chemical processes of which the most widely used is solvent extraction using diethanolamine (DEA). A mixture of diethanolamine and water trickles down a contactor containing with trays or packing that distribute the liquid, while the gas stream containing the hydrogen sulfide enters at the base of the contactor. The diethanolamine selectively absorbs the hydrogen sulfide after which the hydrogen sulfide-rich (fat) diethanolamine is then fractionated to separate the hydrogen sulfide that is sent to a sulfur recovery plant and the stripped (lean) diethanolamine recycled.

The conversion of hydrogen sulfide to sulfur is accomplished by means of the Claus process, and, although there are variations on the process, most options use a two-stage, split-stream process. In the first stage, part of the hydrogen sulfide stream is burned in a furnace in a limited supply of oxygen to produce not only sulfur dioxide and water but also sulfur.



The remainder of the hydrogen sulfide is mixed with the combustion products and passed over a catalyst. The hydrogen sulfide reacts with the sulfur dioxide to form sulfur and water:



Thus, Claus plants convert approximately 90% to 93% of the hydrogen sulfide to sulfur, and removal of the remaining sulfur can be achieved by use of more advanced processes, such as (for example) the Stretford process.

See also: Gas Cleaning, Hydrogen Sulfide, Hydrogen Sulfide Control, Hydrogen Sulfide Conversion.

Hydrogeology

Hydrogeology is the branch of science that deals with the occurrence and movement of subterranean water, and it is a subdivision of the science of hydrology that deals with the water beneath the surface of the Earth. It is interdisciplinary in scope in that it involves the application of the physical, biological, and mathematical sciences. Because hydrogeology deals with the occurrence and movement of water in an almost infinitely complex subsurface geologic environment, it is, in its most advanced state, one of the most complex of the sciences. On the other hand, many of the basic principles and methods of hydrogeology can be understood readily and used in the solution of groundwater problems.

The relevance of the science of hydrogeology is becoming more relevant where overexploitation, declining groundwater levels, and groundwater quality issues are affecting the lives of most of the population. Thus, good understanding and successful application of this science by the practitioners is of critical importance to the welfare of the environment.

Hydrokinetic Energy

Hydrokinetic energy is the energy generated by the movement of a body of water. The Earth's tides, waves, ocean currents, and free-flowing rivers contain an untapped, powerful, highly-concentrated and clean energy resource. Traditional hydropower (river dams and conduits) is also produced by moving water. A variety of hydrokinetic energy sources are described below.

This class of renewable energy technology is being strongly recognized as a unique and unconventional solution that falls within the realms of both in-land water resource and marine energy. In contrast to conventional hydroelectric plants, where an artificial water-head is created using dams or penstocks (for large-hydro and micro-hydro, respectively), hydrokinetic converters are constructed without significantly altering the natural pathway of the water stream. With regard to ocean power utilization, these technologies can be arranged in multi-unit array that would

extract energy from tidal and marine currents as opposed to tidal barrages where stored potential energy of a basin is harnessed.

In-stream hydrokinetic projects generate electricity directly from the flow of water in rivers, inland waterways, irrigation canals, and other man-made conduits. Energy-generating mechanisms may be placed as individual units or in arrays. They may be submerged, floating, or tethered to existing structures like bridge abutments or other in-water infrastructure. Some are placed downstream from existing hydropower projects.

In-stream hydrokinetic projects generate energy from the horizontal flow of water. These energy-generating projects use a variety of technologies, including the following: (i) horizontal axis turbines, (ii) vertical axis turbines, and (iii) helical turbines that may be either vertical or horizontal. As the water current passes through the turbine (rotor fan), the turbine rotates on a shaft connected to the generator. The rotational speed is proportional to the velocity of the fluid.

Horizontal axis turbines may look much like wind turbines, and they extract kinetic energy from the moving water in the same way that wind turbines extract energy from moving air. Sometimes, the rotor is enclosed inside a duct (often funnel-shaped) to concentrate the flow past the turbine. This may allow operation over a greater range of current velocities and generate more electricity per unit of rotor area. In vertical axis turbines, the axis of the rotor is oriented perpendicular to the flow. Vertical axis turbines may take many different forms and also may be enclosed within a duct.

The ocean produces two different types of energy which are (i) the thermal energy from the heat of the Sun, and (ii) the mechanical energy derived from the tides and waves. Tides are driven primarily by the gravitational pull of the moon, and waves are driven primarily by winds. Tides and waves are therefore intermittent sources of energy, while ocean thermal energy (from the sun) is fairly constant. The electricity conversion of both tidal and wave energy usually involves mechanical devices.

Wave power devices extract energy directly from the surface motion of powerful ocean waves or from pressure fluctuations below the surface. A variety of technologies have been proposed to capture wave energy. Some of the more promising designs are now being tested at commercial scales. Wave technologies have been designed for near-shore, offshore, and far offshore locations. All wave energy technologies are intended to be installed at or near the water's surface, in waters more than 40 meters deep. These technologies differ in their orientation to the waves with which they are interacting and the manner in which they convert wave energy into electricity.

Tidal and ocean current energy can be exploited by the following: (i) building semi-permeable barrages (dam-like structures) across estuaries with a high tidal range, or (ii) harnessing offshore tidal streams. Unlike wind and waves, tidal and ocean currents are fairly predictable. During high tides, barrages allow tidal waters to fill an estuary through sluices which then close when the tide begins to fall. Once the tide is low enough, the stored water is released at pressure through turbines.

Tidal energy may be harnessed using offshore underwater devices similar to wind turbines. Submerged rotating devices capture energy through the processes of hydrodynamic lift or drag. These devices consist of rotor blades, a generator for converting the rotational energy into electricity, and a means for transporting the electrical current to the on-shore electrical grid. Submerged turbines can have either a horizontal or vertical axis of rotation. Mechanisms such as posts, cables, or anchors are required to keep the turbines stationary relative to the tidal currents. Prototype horizontal axis turbines, similar to wind turbines, have been built and tested. Vertical axis turbine designs have been proposed, with some designs resembling egg beaters.

Turbines may be anchored to the ocean floor in a variety of ways. They may be tethered with cables, using the relatively constant current interacting with the turbine to maintain location and stability. Imagine an underwater kite flying, where the kite is the upright turbine and the kite flyer is the anchor. The system may also include concentrators (or shrouds) around the blades to increase the flow and power output from the turbine. Another proposed design is mooring a barge in the current stream with a large cable loop to which water-filled parachutes are fastened. The parachutes would be pushed by the current and then closed on their way back, forming a loop similar to a large horizontal waterwheel. In large areas with powerful currents, it may be possible to install water turbines in groups or clusters to create a "marine energy facility" (similar to a wind energy facility). Turbine spacing would be determined based on wake interactions and maintenance needs.

Hydrokinetic Power Generation

Hydrokinetic energy converters can tap into three types of resources: (i) inland rivers, (ii) tidal estuaries and channels, and (iii) ocean currents.

Axial-flow systems

The vast majority of the hydrokinetic energy converter system are lift-based, axial-flow, tidal turbines. Drag-based systems typically have lower efficiencies compared to lift-based systems. However, drag-based systems can be useful in extracting energy from flows with exceptional amounts of debris, which is an important consideration for some sites. Lift-based, axial-flow turbines use the same principles as aircraft wings, propellers, and wind turbines. The blades of a lift-based turbine are composed of two-dimensional hydrofoil cross sections.

Cross-flow systems

Cross-flow turbines rely on the same principles as lift-based axial flow turbines to develop a pressure differential across blade-sections. However, cross-flow systems orient the axis of rotation normal to the freestream (versus parallel to the free stream for axial-flow systems). Therefore, as across-flow turbines rotate, the angle of attack of each blade varies cyclically. The cyclical variation of the angle of attack creates cyclical blade loading, which increases the fatigue experienced by the blades. Much of the cyclical loading can be alleviated by using helical instead of straight blades.

Though cross-flow turbines are generally less efficient than axial-flow turbines, they do have some distinct advantages: cross-flow turbines can have a rectangular cross section, which allows them to be more efficiently packed in arrays than circular-cross-section axial-flow turbines. Another benefit is the ability to generate power from any flow direction that is perpendicular to the axis, which is extremely advantageous in a tidal flow.

Oscillating systems

Oscillating systems using flapping foils tend to suffer from a complex control system, which is necessary to maintain the wing's optimal angle of attack to create enough lift for power production. The control system is also required to overcome the pitching moment of the wing and reverse the direction of oscillation. The most successful oscillating system uses vortex-induced vibrations to generate energy. Vortex-induced vibrations occur due to the periodic shedding of vortices in the wake of a bluff body.

Hydrologic Cycle

The term hydrologic cycle refers to the continuous movement of water above, on, and below the surface of the Earth. The concept of the hydrologic cycle is central to an understanding of groundwater supplies. Although the hydrologic cycle has neither a beginning nor an end, it is convenient to discuss the principal features by starting with evaporation from vegetation, from exposed moist surfaces including the land surface and from the ocean.

The Sun warms the earth and oceans, causing water to evaporate and enter the air. Plants also release water into the air through a process called transpiration. As this moisture rises, it cools and condenses to form clouds. These clouds release water as precipitation in the form of rain, sleet, hail, and snow. This precipitation is partly intercepted in its downward movement before it falls on the surface from where part of it infiltrates or runs off, while the rest enter lakes and streams directly. All water on the land surface is surface water. Water that infiltrates, fills the space between particles of soil, sand, and rocks in the earth, thus forming groundwater. Groundwater, which flows very slowly, and surface water, which flows quickly, both move toward the oceans. Plants, animals, and people use some water, and some is returned to the air through transpiration. The remainder returns to the oceans where it again evaporates to repeat the hydrologic cycle.

See also: Biogeochemical Cycles, Water Cycle.

Hydrolysis and Fermentation of Sugar

The use of sugar and starch crops to produce ethanol through fermentation is well known, but has certain limits: The crops has high value for food application, and their sugar yield per hectare is low compared to the most prevalent forms of sugar in nature: cellulose and hemicellulose. The potential of lignocellulosic biomass is therefore considerably larger than crops and starch, and is especially well suited in Northern parts of the world with less Sun radiation.

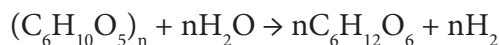
Pre-treatment is necessary to remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity of the materials. Pre-treatment technologies are diverse and numerous, but might be categorized in four main groups which are (i) physical pretreatment, (ii) pyrolysis, (iii) ozonolysis, and (iv) biological pretreatment.

The different pre-treatments have their specific advantages and disadvantages, and are at different stages of development. The choice of pre-treatment technology heavily influences cost and performance in subsequent hydrolysis and fermentation.

See also: Fermentation, Starch, Steam Explosion.

Hydrolysis – Anaerobic Digestion

Chemically, the term hydrolysis refers to the cleavage of chemical bonds by the addition of water. Cations and anions react with water molecules, altering pH in the process to create cleavage of H–O bonds. Hydrolysis is the first step in the anaerobic digestion process. It is a relatively slow step that can limit the rate of the overall digestion process, especially when solid waste substrates are used; the reaction associated with this step is:



The reaction is catalyzed by homogeneous or heterogeneous acids to yield a fermentable monosaccharide, glucose ($\text{C}_6\text{H}_{12}\text{O}_6$).

The usefulness of this reaction relates to the fact that the glucose can undergo further successive reactions to produce compounds such as formic acid (HCO_2H , also known as methanoic acid), hydroxymethyl furfural ($\text{C}_6\text{H}_6\text{O}_3$, also known as 5-furfural), and levulinic acid ($\text{C}_5\text{H}_8\text{O}_3$, also known as 4-oxopentanoic acid), which are valuable organic compounds used in the manufacture of a variety of other compounds.

See also: Acetogenesis, Acidogenesis, Methanogenesis.

Hydrolysis – Lignocellulosic Materials

Acid hydrolysis of plant lignocellulosic biomass has been known since 1819 – examples are the modified Bergius process (40% HCl) operated during World War II in Germany, and the more recently modified Scholler processes (0.4% H_2SO_4) in the former Soviet Union, Japan, and Brazil. Acid hydrolysis can be performed with several types of acids, including (alphabetically) formic acid, hydrochloric acid, hydrofluoric acid, nitric acid, phosphoric acid, sulfuric acid, and sulfurous acid either in concentrated or diluted form.

Processes involving concentrated acids are operated at low temperature and give high yields (on the order of 90% w/w of theoretical glucose yield), but the large amount of acids used causes problems associated with equipment corrosion and energy-demanding acid recovery.

The main advantage of dilute acid hydrolysis is the relatively low acid consumption. However, high temperatures are required to achieve acceptable rates of conversion of cellulose to glucose, and high temperatures also increase the rates of hemicellulose sugar decomposition and equipment corrosion. Sugar degradation products can also cause inhibition in the subsequent fermentation stage. The maximum yield of glucose is obtained at high temperature and short residence time, but even under these conditions, the glucose yield is only between 50% and 60% of the theoretical value.

A two-stage process has been developed to decrease sugar degradation. In the first hydrolysis stage, the relatively easily hydrolyzed hemicellulose is released under mild conditions. This enables the second acid hydrolysis step to proceed under harsher conditions without degrading the hemicellulose sugars to furfural, hydroxymethyl-furfural, and other degradation products. Using a two-stage dilute acid hydrolysis process, recovery yields of as much as 70 to 98% of the xylose, galactose, mannose, and arabinose from softwood is possible. However, the yield of glucose was still low at 50%.

See also: Acid Hydrolysis, Concentrated Acid Hydrolysis.

Hydropower

The energy of falling water and running water can be utilized to provide *water power* or *hydropower*, which is the form of renewable energy derived from the gravitational force of falling or flowing water harnessed for useful purposes. Since ancient times, hydropower has been used for irrigation and the operation of various mechanical devices, such as watermills, sawmills, textile mills, dock cranes, domestic lift, and power houses.

Since the early twentieth century, the term hydropower has been used almost exclusively in conjunction with the modern development of hydroelectric power, which allowed use of distant energy sources. Hydroelectricity is the term referring to electricity generated by hydropower, the production of electrical power through the use of the gravitational force of falling or flowing water. Another method used to transmit energy involves a *trompe*: a water-powered gas compressor, commonly used before the advent of the electric-powered compressor, which is somewhat like an airlift pump working in reverse. A *trompe* produces compressed air from falling water. Compressed air could then be piped to power other machinery at a distance from the waterfall.

Understanding the water cycle is important to understanding hydropower. The water cycle has three steps: (i) solar energy heats water on the surface of rivers, lakes, and oceans, which causes the water to evaporate, (ii) water vapor condenses into clouds and falls as precipitation – rain and snow, and (iii) precipitation collects in streams and rivers, which empty into oceans and lakes, where it evaporates and begins the cycle again.

The amount of precipitation that drains into rivers and streams in a geographic area determines the amount of water available for producing hydropower. Seasonal variations in precipitation and long-term changes in precipitation patterns, such as droughts, can have large effects on the availability of hydropower production.

Because the source of hydroelectric power is water, hydroelectric power plants are usually located on or near a water source. The volume of the water flow and the change in elevation – or fall, and often referred to as *head* – from one point to another determine the amount of available energy in moving water. In general, the greater the water flow and the higher the head, the more electricity a hydropower plant can produce. At hydropower plants, water flows through a pipe, or *penstock*, then pushes against and turns blades in a turbine to spin a generator to produce electricity.

Run-of-the-river systems are systems where the force of the river's current applies pressure on a turbine. The facilities may have a *weir* in the water course to divert water flow to hydro turbines. *Storage systems* are systems where water accumulates in reservoirs created by dams on streams and rivers and is released through hydro turbines as needed to generate electricity. Most U.S. hydropower facilities have dams and storage reservoirs.

Pumped-storage hydropower facilities are a type of hydroelectric storage system where water is pumped from a water source up to a storage reservoir at a higher elevation and is released from the upper reservoir to power hydro turbines located below the upper reservoir. The electricity for pumping may be supplied by hydro turbines or by other types of power plants including fossil fuel or nuclear power plants. They usually pump water to storage when electricity demand and generation costs, and/or when wholesale electricity prices are relatively low and release the stored water to generate electricity during peak electricity demand periods when wholesale electricity prices are relatively high. Pumped-storage hydroelectric systems generally use more electricity to pump water to the upper water storage reservoirs than they produce with the stored water. Therefore, pumped-storage facilities have net negative electricity generation balances.

See also: Hydrokinetic Energy, Hydrokinetic Power Generation.

Hydroprocessing

Hydroprocessing is a term often equally applied to hydrotreating and to hydrocracking – also often collectively applied to both types of processes.

The use of hydrogen in thermal processes uses the principle that the presence of hydrogen during a thermal reaction of a petroleum feedstock will terminate many of the coke-forming reactions and enhance the yields of the lower-boiling products. Hydrogenation processes for the conversion of various feedstocks may be classified as (i) destructive hydrogenation and (ii) nondestructive hydrogenation.

Destructive hydrogenation (hydrogenolysis or hydrocracking) is characterized by the conversion of the higher-molecular-weight constituents in a feedstock to lower-boiling products. Such treatment requires severe processing conditions and the use of high hydrogen pressures to minimize polymerization and condensation reactions that lead to coke formation.

Nondestructive or simple hydrogenation is generally used for the purpose of improving product quality without appreciable alteration of the boiling range. Mild processing conditions are employed so that only the more unstable materials are attacked. Nitrogen, sulfur, and oxygen compounds undergo reaction with the hydrogen to remove ammonia, hydrogen sulfide, and water, respectively. Unstable compounds which might lead to the formation of gums, or insoluble materials, are converted to more stable compounds.

See also: Hydrocracking, Hydrotreating, Refining.

Hydroshear Emulsification

Hydroshear emulsification can be used to produce emulsions of diesel-alcohol. However, the emulsion can only remain stable for 45 seconds and, 12% v/v alcohol (energy basis) is the maximum percentage. In the hydro-shear emulsifier (sometimes referred to as a homogenizer), the premixed liquids are pumped into a cylindrical chamber at relatively low pressure. The liquids enter the chamber through a tangential port at its center and exit via two cone-shaped discharge nozzles at the ends of the chamber and accelerate to a high velocity as they enter the chamber, spread out to cover the full width of the chamber wall and flow toward the center, rotating in ever-decreasing circles. High shear develops between the adjacent layers of liquid, destabilizing the large droplets of the internal phase. In the center of the cylinder, a zone of low pressure develops and cavitation, ultrahigh frequency vibration, and shock waves occur which all contribute to the breakup of the droplets and the formation of an emulsion.

See also: Alcohol-Diesel Emulsion

Hydrothermal Upgrading

The hydro thermal upgrading process (HTU process) converts biomass in the presence of water. Liquefaction takes place at moderate temperatures at, high pressure with the addition of hydrogen. The interest in liquefaction is low because the reactors and fuel feeding systems are more complex and more expensive than for pyrolysis processes.

In the hydrothermal upgrading process (HTU process), biomass is treated for 5-20 min in water at temperatures of 300 to 360°C (570 to 650°F) and pressure of 1,500 to 2,650 psi. As a result, most of the oxygen is removed from the biomass feedstock, mainly as carbon dioxide and – and to a lesser extent – as water. The product obtained is a high-boiling organic liquid with 10 to 20% oxygen content on weight basis. The claimed thermal efficiency of the conversion process is 75 to 80%. The properties of the HTU product (biocrude) resemble those of crude oil (Table H-6).

Table H-6 Feedstocks and products for the hydrothermal upgrading process.

Feedstocks	Descriptors
Biomass	Agricultural residue Domestic residue Municipal solid waste Sewage sludge Wood and forest waste
Process parameters	Reaction medium: water Temperature: 300-350°C (570-660°F) Pressure: 1,700 to 2,600 psi Residence time: 5-20 minutes (feedstock dependent)
Process chemistry	Decarboxylation Dehydration Depolymerization Hydrodeoxygenation Hydrogenation
Products (% w/w on feedstock)	Bio-oil (biocrude): 45 Gas: 25 Water-soluble organic products: 10 Other: 20

In principle, biocrude could be fed into an entrained flow gasifier, similar to pyrolysis slurry. Nevertheless, it is more often considered for further upgrading via catalytic hydrodeoxygenation (HDO) to middle distillate products (kerosene, diesel) and refinery feedstock.

The main advantage of the hydrothermal upgrading process is its suitability for wet biomass. Nonetheless, considering that the entrained flow gasification releases as by-product a lot of waste heat, which anyhow has to find useful application, this advantage becomes less important.

See also: Biomass – Pyrolysis.

Hydrotreating

Hydrotreating is a catalytic hydrogenation process used to remove approximately 90% of contaminants such as nitrogen, sulfur, oxygen, and metals from liquid petroleum fractions. These contaminants, if not removed from the petroleum fractions as they travel through the refinery processing units, can have detrimental effects on the equipment, the catalysts, and the quality of the finished product. Typically, hydrotreating is done prior to processes such as catalytic reforming so that the catalyst is not contaminated by untreated feedstock. Hydrotreating is also used prior to catalytic cracking to reduce sulfur and improve product yields, and to upgrade middle-distillate petroleum fractions into finished kerosene, diesel fuel, and heating fuel oils. In addition, hydrotreating converts olefins and aromatics to saturated compounds.

The increasing importance of hydrosulfurization (HDS) and hydrodenitrogenation (HDN) in petroleum processing in order to produce clean-burning fuels has led to a surge of research on the chemistry and engineering of heteroatom removal, with sulfur removal being the most prominent area of research. Most of the earlier works are focused (i) on catalyst characterization by physical methods, (ii) on low-pressure reaction studies of model compounds having relatively high reactivity, (iii) on process development, or (iv) on cobalt-molybdenum – Co-Mo – catalysts, nickel-molybdenum catalysts – Ni-Mo – or nickel-tungsten – Ni-W – catalysts supported on alumina, often doped by fluorine or phosphorus.

Hydrodesulfurization and demetallization occur simultaneously on the active sites within the catalyst pore structure. Sulfur and nitrogen occurring in residua are converted to hydrogen sulfide and ammonia in the catalytic reactor, and these gases are scrubbed out of the reactor effluent gas stream. The metals in the feedstock are deposited on the catalyst in the form of metal sulfides, and cracking of the feedstock to distillate produces a laydown of carbonaceous material on the catalyst; both events poison the catalyst, and activity or selectivity suffers. The deposition of carbonaceous material is a fast reaction that soon equilibrates to a particular carbon level and is controlled by hydrogen partial pressure within the reactors. On the other hand, metal deposition is a slow reaction that is directly proportional to the amount of feedstock passed over the catalyst.

Basic nitrogen-containing compounds in a feed diminish the cracking activity of hydrocracking catalysts. However, zeolite catalysts can operate in the presence of substantial concentrations of ammonia, in marked contrast to silica-alumina catalysts, which are strongly poisoned by ammonia. Similarly, sulfur-containing compounds in a feedstock adversely affect the noble metal hydrogenation component of hydrocracking catalysts. These compounds are hydrocracked to hydrogen sulfide, which converts the noble metal to the sulfide form. The extent of this conversion is a function of the hydrogen and hydrogen sulfide partial pressures.

Removal of sulfur from the feedstock results in a gradual increase in catalyst activity, returning almost to the original activity level. As with ammonia, the concentration of the hydrogen sulfide can be used to precisely control the activity of the catalyst. Non-noble metal-loaded zeolite catalysts have an inherently different response to sulfur impurities since a minimum level of hydrogen sulfide is required to maintain the nickel-molybdenum and nickel-tungsten in the sulfide state.

The character of the hydrotreating processes is chemically simple since they essentially involve removal of sulfur and nitrogen as hydrogen sulfide and ammonia, respectively:



However, nitrogen is the most difficult contaminant to remove from feedstocks, and processing conditions are usually dictated by the requirements for nitrogen removal.

In general, any catalyst capable of participating in hydrogenation reactions may be used for hydrodesulfurization. The sulfides of hydrogenating metals are particularly used for hydrodesulfurization, and catalysts containing cobalt, molybdenum, nickel, and tungsten are widely used on a commercial basis.

Different rates of reaction may occur with various types and concentrations of metallic compounds. For example, a medium metal-content feedstock will generally have a lower rate of demetallization compared to high-metal content feedstock. And, although individual organometallic compounds decompose according to both first- and second-order rate expressions, for reactor design, a second-order rate expression is applicable to the decomposition of residuum as a whole.

Generally, it is more economical to hydrotreat high-sulfur feedstocks before catalytic cracking than to hydrotreat the products from catalytic cracking. The advantages are (i) the products require less finishing, (ii) the sulfur is removed from the catalytic cracking feedstock, and corrosion is reduced in the cracking unit, (iii) the potential for coke formation during cracking is reduced and higher conversions result, and (iv) the quality of the gas oil fraction is improved.

Although hydrocracking will occur during hydrotreating, attempts are made to minimize such effects, but the degree of cracking is dependent on the nature of the feedstock.

See also: Hydrocracking, Hydrodenitrogenation, Hydrodesulfurization, Refining.

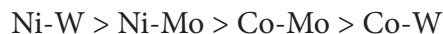
Hydrotreating Catalysts

Hydrotreating catalysts are usually cobalt-molybdenum catalysts and under the conditions whereby nitrogen removal is accomplished, desulfurization usually occurs as well as oxygen removal. Indeed, it is generally recognized

that fullest activity of the hydrotreating catalyst is not reached until some interaction with the sulfur (from the feedstock) has occurred, with part of the catalyst metals converted to the sulfides. Too much interaction may of course lead to catalyst deactivation.

A wide variety of metals are active hydrogenation catalysts; those of most interest are nickel, palladium, platinum, cobalt, iron, nickel-promoted copper, and copper chromite. Special preparations of the first three are active at room temperature and atmospheric pressure. The metallic catalysts are easily poisoned by sulfur-containing and arsenic-containing compounds, and even by other metals. To avoid such poisoning, less effective but more resistant metal oxides or sulfides are frequently employed, generally those of tungsten, cobalt, chromium, or molybdenum.

For hydrotreating of feedstocks that contain appreciable concentrations of sulfur and nitrogen, sulfided nickel-molybdenum (Ni-Mo), nickel-tungsten (Ni-W), or cobalt-molybdenum (Co-Mo) on alumina (γ -Al₂O₃) catalysts are generally used, whereas supported noble metal catalysts have been used for sulfur- and nitrogen-free feedstocks. Catalysts containing noble metals on Y-zeolites have been reported to be more sulfur tolerant than those on other supports. Within the series of cobalt-promoted or nickel-promoted group VI metal (Mo or W) sulfides supported on γ -Al₂O₃, the ranking for hydrogenation is:



Nickel-tungsten (Ni-W) and nickel-molybdenum (Ni-Mo) on Al₂O₃ catalysts are widely used to reduce sulfur, nitrogen, and aromatics levels in petroleum fractions by hydrotreating.

The poisoning effect of nitrogen can be offset to a certain degree by operation at a higher temperature. However, the higher temperature tends to increase the production of material in the methane (CH₄) to butane (C₄H₁₀) range and decrease the operating stability of the catalyst so that it requires more frequent regeneration. Catalysts containing platinum or palladium (approximately 0.5% wet) on a zeolite base appear to be somewhat less sensitive to nitrogen than are nickel catalysts, and successful operation has been achieved with feedstocks containing 40 ppm nitrogen. This catalyst is also more tolerant of sulfur in the feed, which acts as a temporary poison, the catalyst recovering its activity when the sulfur content of the feed is reduced.

On such catalysts as nickel or tungsten sulfide on silica-alumina, isomerization does not appear to play any part in the reaction, as uncracked normal paraffins from the feedstock tend to retain their normal structure. Extensive splitting produces large amounts of low-molecular-weight (C₃-C₆) paraffins, and it appears that a primary reaction of paraffins is catalytic cracking followed by hydrogenation to form iso-paraffins. With catalysts of higher hydrogenation activity, such as platinum on silica-alumina, direct isomerization occurs. The product distribution is also different, and the ratio of low- molecular-weight to intermediate-molecular-weight paraffins in the breakdown product is reduced.

In addition to the chemical nature of the catalyst, the physical structure of the catalyst is also important in determining the hydrogenation and cracking capabilities, particularly for viscous feedstocks. When gas oils and residua are used, the feedstock is present as liquids under the conditions of the reaction. Additional feedstock and the hydrogen must diffuse through this liquid before reaction can take place at the interior surfaces of the catalyst particle.

At high temperatures, reaction rates can be much higher than diffusion rates and concentration gradients can develop within the catalyst particle. Therefore, the choice of catalyst porosity is an important parameter. When feedstocks are to be hydrocracked to liquefied petroleum gas and gasoline, pore diffusion effects are usually absent. High surface area (approximately 300 m²/g) and low-to-moderate porosity (from 12 D pore diameter with crystalline acidic components to 50 D or more with amorphous materials) catalysts are used. With reactions involving high-molecular-weight feedstocks, pore diffusion can exert a large influence, and catalysts with pore diameters greater than 80 D are necessary for more efficient conversion.

Catalyst operating temperature can influence reaction selectivity since the activation energy for hydrotreating reactions is much lower than for hydrocracking reaction. Therefore, raising the temperature in a residuum hydrotreater increases the extent of hydrocracking relative to hydrotreating, which also increases the hydrogen consumption.

The life of a catalyst used to hydrotreat petroleum residua is dependent on the rate of carbon deposition and the rate at which organometallic compounds decompose and form metal sulfides on the surface. Several different metal complexes exist in the asphaltene fraction of the residuum, and an explicit reaction mechanism of decomposition that would be a perfect fit for all of the compounds is not possible. However, in general, terms, the reaction can be described as hydrogen which is (i) dissolved in the feedstock contacting an organometallic compound, (ii) at the surface of the hydrotreating catalyst and producing a metal sulfide, and (iii) producing a hydrocarbon derivative.

Molybdenum sulfide (MoS_2), usually supported on alumina, is widely used in petroleum processes for hydrogenation reactions. It is a layered structure that can be made much more active by addition of cobalt or nickel. When promoted with cobalt sulfide (CoS), making what is called cobalt-molybdenum catalysts, it is widely used in hydrodesulfurization (HDS) processes. The nickel sulfide (NiS)-promoted version is used for hydrodenitrogenation (HDN) as well as hydrodesulfurization (HDS). The closely related tungsten compound (WS_2) is used in commercial hydrocracking catalysts. Other sulfides (iron sulfide, FeS , chromium sulfide, Cr_2S_3 , and vanadium sulfide, V_2S_5) are also effective and used in some catalysts. A valuable alternative to the base metal sulfides is palladium sulfide (PdS). Although it is expensive, palladium sulfide forms the basis for several highly active catalysts.

Catalyst poisoning can be minimized by mild hydrogenation to remove nitrogen, oxygen, and sulfur from feedstocks in the presence of more resistant catalysts, such as cobalt-molybdenum-alumina ($\text{Co-Mo-Al}_2\text{O}_3$). The reactions involved in nitrogen removal are somewhat analogous to those of the sulfur compounds and follow a stepwise mechanism to produce ammonia and the relevant substituted aromatic compound.

One of the chief problems with hydroprocessing residua is the deposition of metals, in particular vanadium, on the catalyst. It is not possible to remove vanadium from the catalyst, which must therefore be replaced when deactivated, and the time taken for catalyst replacement can significantly reduce the unit time efficiency. Fixed-bed catalysts tend to plug owing to solids in the feed or carbon deposits when processing residual feeds.

See also: Hydrotreating Catalysts, Hydrotreating Processes, Hydrotreating Process Parameters.

Hydrotreating Processes

Hydrotreating technology is one of the most commonly used refinery processes, designed to remove contaminants such as sulfur, nitrogen, condensed ring aromatics, or metals. The feedstocks used in the process range from naphtha to vacuum resid, and the products in most applications are used as environmentally acceptable clean fuels. Hydrotreating technology has a long history of commercial application since 1950s, with more than 500 licensed units placed in operation worldwide. Furthermore, recent regulatory requirements to produce ultra-low-sulfur diesel (ULSD) and gasoline have created a very dynamic market as refiners must build new or revamp their existing assets to produce the low-sulfur, even no-sulfur fuels.

Hydrotreating is carried out by charging the feed to the reactor, together with a portion of all the hydrogen produced in the catalytic reformer. Suitable catalysts are tungsten-nickel sulfide, cobalt-molybdenum-alumina, nickel oxide-silica-alumina, and platinum-alumina. Most processes employ cobalt-molybdenum catalysts, which generally contain approximately 10% by weight molybdenum oxide and less than 1% by weight cobalt oxide supported on alumina. The temperatures employed are in the range of 300 to 345°C (570 to 850°F), and the hydrogen pressures are approximately 500 to 1,000 psi.

For distillate feedstocks, the reaction generally takes place in the vapor phase but, depending on the application, may be a mixed-phase reaction. The reaction products are cooled in a heat exchanger and led to a high-pressure separator where hydrogen gas is separated for recycling. Liquid products from the high-pressure separator flow to a low-pressure separator (stabilizer) where dissolved gases are removed. The product may then be fed to a reforming or cracking unit if desired. As a note, the crude oil refining industry often employs two-stage processes in which the feedstock undergoes both hydrotreating and hydrocracking (Figure H-2).

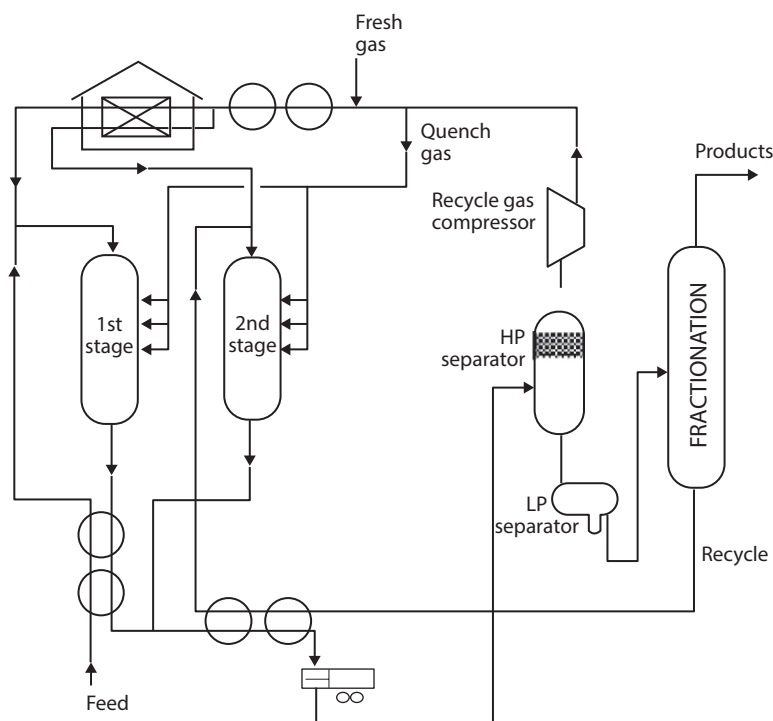


Figure H-2 Two-stage hydrotreating.

In the first, or pretreating, stage, the main purpose is conversion of nitrogen compounds in the feed to hydrocarbon derivatives and to ammonia by hydrogenation and mild hydrocracking. Typical conditions are 340 to 930°C (650 to 1,740°F), 150 to 2,500 psi (1 to 17 MPa), and a catalyst contact time of 0.5 to 1.5 h; up to 1.5% w/w hydrogen is absorbed, partly by conversion of the nitrogen compounds but chiefly by aromatic compounds that are hydrogenated. It is most important to reduce the nitrogen content of the product oil to less than 0.001% w/w (10 parts per million). This stage is usually carried out with a bifunctional catalyst containing hydrogenation promoters, for example, nickel and tungsten or molybdenum sulfides, on an acid support, such as silica-alumina.

The metal sulfides hydrogenate aromatics and nitrogen compounds and prevent deposition of carbonaceous deposits; the acid support accelerates nitrogen removal as ammonia by breaking carbon-nitrogen bonds. The catalyst is generally used as 1/8 x 1/8 inch (0.32 x 0.32 cm) or 1/16 X 1/8 inch (0.16 x 0.32 cm) pellets, formed by extrusion.

Most of the hydrotreating cracking is accomplished in the first stage. Ammonia and some gasoline are usually removed from the first-stage product, and then the remaining first-stage product, which is low in nitrogen compounds, is passed over the second-stage catalyst. Again, typical conditions are 300 to 370°C (600 to 700°F), 1,500 to 2,500 psi (10 to 17 MPa) hydrogen pressure, and 0.5 to 1.5 h contact time; 1 to 1.5% w/w hydrogen may be absorbed. Conversion to gasoline or jet fuel is seldom complete in one contact with the catalyst, so the lower-boiling constituents are removed by distillation of the products and the heavier, higher-boiling product combined with fresh feed and recycled over the catalyst until it is completely converted.

See also: Refining.

Hydrotreating – Process Parameters

All hydrotreating processes react hydrogen with a hydrocarbon feedstock to produce hydrogen sulfide and a hydrocarbon product free of heteroatoms and metals.

In the process, the feedstock is preheated and mixed with hot recycle gas containing hydrogen and the mixture is passed over the catalyst in the reactor section at temperatures between 290 to 450°C (550 to 850°F) and pressures between 150 and 3,000 psig (1 to 20.7 MPa gauge). The reactor effluent is then cooled by heat exchange, and desulfurized liquid hydrocarbon product and recycle gas are separated at essentially the same pressure as used in the reactor. The recycle gas is then scrubbed and/or purged of the hydrogen sulfide and low-boiling hydrocarbon gases, mixed with fresh hydrogen makeup, and preheated prior to mixing with hot hydrocarbon feedstock.

The recycle gas scheme is used in the hydrodesulfurization process to minimize physical losses of expensive hydrogen. Hydrodesulfurization reactions require a high hydrogen partial pressure in the gas phase to maintain high desulfurization reaction rates and to suppress carbon laydown (catalyst deactivation). The high hydrogen partial pressure is maintained by supplying hydrogen to the reactors at several times the chemical hydrogen consumption rate. The majority of the unreacted hydrogen is cooled to remove hydrocarbon derivatives, recovered in the separator, and recycled for further utilization. Hydrogen is physically lost in the process by solubility in the desulfurized liquid hydrocarbon product, and from losses during the scrubbing or purging of hydrogen sulfide and low-boiling hydrocarbon gases from the recycle gas.

The operating conditions in distillate hydrodesulfurization are dependent upon the feedstock as well as the desired degree of desulfurization or quality improvement. Kerosene and low-boiling gas oils are generally processed at mild severity and high throughput, whereas low-boiling catalytic cycle oils and thermal distillates require slightly more severe conditions. Higher-boiling distillates, such as vacuum gas oils and lube oil extracts, require the most severe conditions.

The principal variables affecting the required severity in distillate desulfurization are: (i) catalyst life, (ii) feedstock properties, (iii) hydrogen partial pressure, (iv) reaction temperature, and (v) space velocity.

Catalyst Life

Catalyst life depends on the charge stock properties and the degree of desulfurization desired. The only permanent poisons to the catalyst are metals in the feedstock that deposit on the catalyst, usually quantitatively, causing permanent deactivation as they accumulate. However, this is usually of little concern except when deasphalted oils are used as feedstocks since most distillate feedstocks contain low amounts of metals. Nitrogen compounds are a temporary poison to the catalyst, but there is essentially no effect on catalyst aging except that caused by a higher temperature requirement to achieve the desired desulfurization. Hydrogen sulfide can be a temporary poison in the reactor gas, and recycle gas scrubbing is employed to counteract this condition.

Providing that pressure drop buildup is avoided, cycles of 1 year or more and an ultimate catalyst life of three years or more can be expected. The catalyst employed can be regenerated by normal steam-air or recycle combustion gas-air procedures. The catalyst is restored to near fresh activity by regeneration during the early part of its ultimate life. However, permanent deactivation of the catalyst occurs slowly during usage and repeated regenerations, so replacement becomes necessary.

Feedstock Properties

The character of the feedstock properties, especially the feed boiling range, has a definite effect on the ultimate design of the desulfurization unit and process flow. In agreement, there is a definite relationship between the percent by weight sulfur in the feedstock and the hydrogen requirements.

In addition, the reaction rate constant in the kinetic relationships decreases rapidly with increasing average boiling point in the kerosene and low-boiling gas oil range but much more slowly in the high-boiling gas oil range. This is attributed to the difficulty in removing sulfur from ring structures present in the entire high-boiling gas oil boiling range.

The hydrodesulfurization of light (low-boiling) distillate (naphtha or kerosene) is one of the more common catalytic hydrodesulfurization processes since it is usually used as a pretreatment of such feedstocks prior to deep hydrodesulfurization or prior to catalytic reforming. This is similar to the concept of pretreating residua prior to hydrocracking to improve the quality of the products. Hydrodesulfurization of such feedstocks is required because sulfur compounds poison the precious-metal catalysts used in reforming and desulfurization can be achieved under relatively mild conditions and is near quantitative. If the feedstock arises from a cracking operation, hydrodesulfurization will be accompanied by some degree of saturation resulting in increased hydrogen consumption.

The hydrodesulfurization of low-boiling (naphtha) feedstocks is usually a gas-phase reaction and may employ the catalyst in fixed beds, and (with all of the reactants in the gaseous phase) only minimal diffusion problems are encountered within the catalyst pore system. It is, however, important that the feedstock be completely volatile before entering the reactor as there may be the possibility of pressure variations (leading to less satisfactory results) if some of the feedstock enters the reactor in the liquid phase and is vaporized within the reactor.

In applications of this type, the sulfur content of the feedstock may vary from 100 ppm to 1% and the necessary degree of desulfurization to be effected by the treatment may vary from as little as 50% to more than 99%. If the sulfur content of the feedstock is particularly low, it will be necessary to pre-sulfide the catalyst. For example, if the feedstock only has 100 to 200 ppm sulfur, several days may be required to sulfide the catalyst as an integral part of the desulfurization process even with complete reaction of all of the feedstock sulfur to, say, cobalt and molybdenum (catalyst) sulfides. In such a case, pre-sulfiding can be conveniently achieved by addition of sulfur compounds to the feedstock or by addition of hydrogen sulfide to the hydrogen.

Generally, hydrodesulfurization of naphtha feedstocks to produce catalytic reforming feedstocks is carried to the point where the desulfurized feedstock contains less than 20 ppm sulfur. The net hydrogen produced by the reforming operation may actually be sufficient to provide the hydrogen consumed in the desulfurization process.

The hydrodesulfurization of middle distillates is also an efficient process, and applications include predominantly the desulfurization of kerosene, diesel fuel, jet fuel, and heating oil that boil over the general range 250 to 400°C (480 to 750°F). However, with this type of feedstock, hydrogenation of the higher-boiling catalytic cracking feedstocks has become increasingly important where hydrodesulfurization is accomplished alongside the saturation of condensed-ring aromatic compounds as an aid to subsequent processing.

Under the relatively mild processing conditions used for the hydrodesulfurization of these particular feedstocks, it is difficult to achieve complete vaporization of the feed. Process conditions may dictate that only part of the feedstock is actually in the vapor phase and that sufficient liquid phase is maintained in the catalyst bed to carry the larger molecular constituents of the feedstock through the bed. If the amount of liquid phase is insufficient for this purpose, molecular stagnation (leading to carbon deposition on the catalyst) will occur.

Hydrodesulfurization of middle distillates causes a more marked change in the specific gravity of the feedstock, and the amount of low-boiling material is much more significant when compared with the naphtha-type feedstock. In addition, the somewhat more severe reaction conditions (leading to a designated degree of hydrocracking) also cause an overall increase in hydrogen consumption when middle distillates are employed as feedstocks in place of the naphtha.

High-boiling distillates, such as the atmospheric and vacuum gas oils, are not usually produced as a refinery product but merely serve as feedstocks to other processes for conversion to lower-boiling materials. For example, gas oils can be desulfurized to remove more than 80% of the sulfur originally in the gas oil with some conversion of the gas oil to lower-boiling materials. The treated gas oil (which has a reduced carbon residue as well as lower sulfur and nitrogen contents relative to the untreated material) can then be converted to lower-boiling products in, say, a catalytic cracker where an improved catalyst life and volumetric yield may be noted.

Hydrogen Partial Pressure

The important effect of hydrogen partial pressure is the minimization of coking reactions. If the hydrogen pressure is too low for the required duty at any position within the reaction system, premature aging of the remaining portion of catalyst will be encountered. In addition, the effect of hydrogen pressure on desulfurization varies with feed boiling range. For a given feed, there exists a threshold level above which hydrogen pressure is beneficial to the desired desulfurization reaction. Below this level, desulfurization drops off rapidly as hydrogen pressure is reduced.

Reaction Temperature

A higher reaction temperature increases the rate of desulfurization at constant feed rate, and the start-of-run temperature is set by the design desulfurization level, space velocity, and hydrogen partial pressure. The capability to increase temperature as the catalyst deactivates is built into the most process or unit designs. Temperatures of 415°C (780°F) and above result in excessive coking reactions and higher than normal catalyst aging rates. Therefore, units are designed to avoid the use of such temperatures for any significant part of the cycle life.

Space Velocity

As the space velocity is increased, desulfurization is decreased, but increasing the hydrogen partial pressure and/or the reactor temperature can offset the detrimental effect of increasing space velocity.

See also: Hydrocracking, Refining.

Hydrous Pyrolysis

Hydrous pyrolysis is the thermal decomposition which takes place when organic compounds are heated to high temperatures in the presence of water. For example, steam cracking is used in the petroleum industry to produce the lower-molecular-weight olefins. Steam cracking uses water in the gas phase, whereas many hydrous pyrolysis processes use superheated water in the liquid phase.

Hydrous pyrolysis could find use in biomass technology and may be a significant process in the creation of shale oil since water under pressure (at high temperature) causes more efficient breakdown of kerogen. Generation and expulsion a bio-oil from biomass shale by hydrous pyrolysis through use of the formation water may provide a means of producing a partially upgraded bio-oil. Minerals may also be anticipated to play a role in hydrous pyrolysis reactions either through a catalytic effect or direct involvement.

Hydroxylation

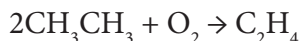
The earliest method for conversion of olefins into alcohols involved their absorption in sulfuric acid to form esters, followed by dilution and hydrolysis, generally with the aid of steam. In the case of ethyl alcohol, the direct catalytic hydration of ethylene can be employed. Ethylene is readily absorbed in 98 to 100% sulfuric acid at 75 to 80°C (165 to 175°F), and both ethyl and diethyl sulfate are formed; hydrolysis takes place readily on dilution with water and heating.

The direct hydration of ethylene to ethyl alcohol is practiced over phosphoric acid on diatomaceous earth or promoted tungsten oxide under 100 psi pressure and at 300°C (570°F):

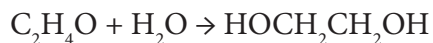


Purer ethylene is required in direct hydration than in the acid absorption process, and the conversion per pass is low, but high yields are possible by recycling. Propylene and the normal butenes can also be hydrated directly.

Ethylene, produced from ethane by cracking, is oxidized in the presence of a silver catalyst to ethylene oxide:



The vast majority of the ethylene oxide produced is hydrolyzed at 100°C to ethylene glycol:



Approximately 70% of the ethylene glycol produced is used as automotive antifreeze, and much of the rest is used in the synthesis of polyesters.

Of the higher alkenes, one of the first alcohol syntheses practiced commercially was that of isopropyl alcohol from propylene. Sulfuric acid absorbs propylene more readily than it does ethylene, but care must be taken to avoid polymer formation by keeping the mixture relatively cool and using acid of approximately 85% strength at 300 to 400 psi pressure; dilution with inert oil may also be necessary. Acetone is readily made from isopropyl alcohol, either by catalytic oxidation or by dehydrogenation over metal (usually copper) catalysts.

Secondary butyl alcohol is formed on absorption of 1-butene or 2-butene by 78 to 80% sulfuric acid, followed by dilution and hydrolysis. Secondary butyl alcohol is converted into methyl ethyl ketone by catalytic oxidation or dehydrogenation.

There are several methods for preparing higher-molecular-weight alcohol derivatives. One method in particular the so-called Oxo reaction and involves the direct addition of carbon monoxide (CO) and a hydrogen (H)

atom across the double bond of an olefin to form an aldehyde (RCH=O), which in turn is reduced to the alcohol (RCH_2OH). Hydroformylation (the Oxo reaction) is accomplished by contacting the olefin with synthesis gas (1:1 carbon monoxide-hydrogen) at 75 to 200°C (165 to 390°F) and 1,500 to 4,500 psi over a metal catalyst, usually cobalt. The active catalyst is held to be cobalt hydrocarbonyl $\text{HCO}(\text{CO})_4$, formed by the action of the hydrogen on dicobalt octacarbonyl.

A wide variety of olefins enter the reaction, those containing terminal unsaturated being the most active. The hydroformylation is not specific; the hydrogen and carbon monoxide add across each side of the double bond. Thus propylene gives a mixture of 60% n-butyraldehyde and 40% iso-butyraldehyde. Terminal (RCH=CH_2) and non-terminal ($\text{RCH=CHR}'$) olefins, such as 1-pentene and 2-pentene, give essentially the same distribution of straight-chain and branched-chain C_6 aldehydes, indicating that rapid isomerization takes place. Simple branched structures add mainly at the terminal carbon; iso-butylene forms 95% iso-valeraldehyde and 5% trimethyl acetaldehyde.

Commercial application of the synthesis has been most successful in the manufacture of iso-octyl alcohol from a refinery C_3 - C_4 copolymer, decyl alcohol from propylene trimer, and tridecyl alcohol from propylene tetramer. Important outlets for the higher alcohols lie in their sulfonation to make detergents and the formation of esters with dibasic acids for use as plasticizers and synthetic lubricants.

The hydrolysis of ethylene chlorohydrin ($\text{HOCH}_2\text{CH}_2\text{Cl}$) or the cyclic ethylene oxide produces ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$). The main use for this chemical is for antifreeze mixtures in automobile radiators and for cooling aviation engines; considerable amounts are used as ethylene glycol dinitrate in low-freezing dynamite. Propylene glycol is also made by the hydrolysis of its chlorohydrin or oxide.

Glycerin can be derived from propylene by high-temperature chlorination to produce alkyl chloride, followed by hydrolysis to allyl alcohol and then conversion with aqueous chloride to glycerol chlorohydrin, a product that can be easily hydrolyzed to glycerol (glycerin).

Glycerin has found many uses over the years; important among these are as solvent, emollient, sweetener, in cosmetics, and as a precursor to nitroglycerin and other explosives.

Hygas Gasifier

The Hygas gasifier, developed by the Institute of Gas Technology, was originally designed to receive a relatively pure hydrogen stream produced in a separate unit.

Three systems were considered: (i) a steam-oxygen gasification system, as in the Hydrane process, (ii) an electrothermal gasification system in which the heat for steam gasification is provided electrically, thus reducing the amount of carbon dioxide to be removed, and (iii) a steam/iron process. The steam/oxygen process has been the method of choice.

The carbon oxides cannot be removed from the steam/oxygen-gasification off gas in the integrated reactor, so the Hygas system is no longer a true hydrogasification process.

The high methane concentrations obtained in the Hydrane process cannot be realized in the integrated Hygas unit due to the lower hydrogen concentrations prevailing. As with the Hydrane system, the Hygas unit has a first dilute-phase stage followed by a second dense-phase fluidized bed stage.

See also: Gasification, Gasification of Biomass, Hydrogasification, Hydrane Gasifier.

Hypro Process

The Hypro process is a continuous catalytic method for hydrogen manufacture from natural gas or from refinery effluent gases. The process is designed to convert natural gas:



Hydrogen is recovered by phase separation to yield hydrogen of approximately 93% purity; the principal contaminant is methane.

See also: Hydrogen Production.

Ideal Gas

An ideal gas is a gas in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces. An ideal gas can be characterized by three variables which are (i) the absolute pressure, P , (ii) the volume, V , and (iii) the absolute temperature, T . The relationship between these variables is called the *ideal gas law*:

$$PV = nRT = NkT$$

In this equation, n is the number of moles, R is the universal gas constant (8.3145 J/mol K), N is the number of molecules, and k is the Boltzmann constant (1.38066×10^{-23}). Thus: $J/K = 8.617385 \times 10^{-5} \text{ eV/K}$ and $k = R/N_A$, where N_A is the Avogadro number ($6.0221 \times 10^{23} / \text{mol}$).

The ideal gas law can arise from the pressure of gas molecules colliding with the walls of a container. And one mole of an ideal gas at standard temperature and pressure occupies 22.4 liters. However, natural gas is a non-ideal gas and does not obey the ideal gas law but obeys the modified gas law:

$$PV = nZRT$$

P is the pressure, V is the volume, T is the absolute temperature (degree Kelvin), Z is the compressibility, n is the number of kilo-moles of the gas, and R is the gas constant.

For example, if all other factors remained constant, when the volume of a certain mass of gas is reduced by 50%, the pressure would double, and so on. As a gas, it would expand to fill any volume it is in. However the compressibility, Z , is the factor which differentiates natural gas from an ideal gas. For methane, Z is 1 at 1 bar but decreases to 0.85 at 100 atmospheres, both at 25°C , that is, it compresses to a smaller volume than the proportional relationship.

Ideal Gas Law

An ideal gas is a gas in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces. An ideal gas can be characterized by three variables: (i) absolute pressure, P , (ii) volume, V , and (iii) absolute temperature, T . The relationship between them is called the *ideal gas law*:

$$PV = nRT = NkT$$

n = number of moles, R = universal gas constant ($= 8.3145 \text{ J/mol K}$), N = number of molecules, k = Boltzmann constant ($= 1.38066 \times 10^{-23} \text{ J/K} = 8.617385 \times 10^{-5} \text{ eV/K}$), $k = R/N_A$, N_A = the Avogadro number $= 6.0221 \times 10^{23} / \text{mol}$.

The ideal gas law can arise from the pressure of gas molecules colliding with the walls of a container. And one mole of an ideal gas at standard temperature and pressure occupies 22.4 liters. However, natural gas is a non-ideal gas and does not obey the ideal gas law but obeys the modified gas law:

$$PV = nZRT$$

P is the pressure, V is the volume, T is the absolute temperature (degree Kelvin), Z is the compressibility, n is the number of kilo-moles of the gas, and R is the gas constant.

For example, if all other factors remained constant, when the volume of a certain mass of gas is reduced by 50%, the pressure would double and so on. As a gas, it would expand to fill any volume it is in. However the compressibility, Z , is the factor which differentiates natural gas from an ideal gas. For methane, Z is 1 at 1 bar but decreases to 0.85 at 100 atmospheres, both at 25°C, that is, it compresses to a smaller volume than the proportional relationship.

The gas deviation factor, z , is close to 1 at low pressures and high temperatures which means the gas behaves as an ideal gas at these conditions. At standard or atmospheric conditions, the gas z factor is always approximately 1. As the pressure increases, the z factor first decreases to a minimum, which is approximately 0.27 for the critical temperature and critical pressure. For temperatures of 1.5 times the critical temperature, the minimum z factor is approximately 0.77 and for temperatures of twice the critical temperature, the minimum z factor is 0.937. At high pressures, the z factor increases above 1 where the gas is no longer super-compressible. At these conditions, the specific volume of the gas is becoming so small and the distance between molecules is much smaller, so that the density is affected by the volume occupied by the individual molecules. Hence, the z factor continues to increase above unity as the pressure increases.

The gas deviation factor, z , is commonly determined by measuring the volume of a sample of the natural gas at a specific pressure and temperature, and then measuring the volume of the same quantity of gas at atmospheric pressure and at a temperature sufficiently high so that the hydrocarbon mixture is in the vapor phase. If the gas deviation factor is not measured, it may be estimated from its specific gravity. The method uses a correlation to estimate pseudo-critical temperature and pseudo-critical pressure values from the specific gravity.

IFPEXOL Process

The IFPEXOL process is a methanol-based process which has the simultaneous capability to dehydrate a gas stream, to remove acid gas from a gas stream, and to control hydrocarbon dew point. More specifically, the IFPEXOL-1 is used for water removal and hydrocarbon dew point control while the IFPEXOL-2 process is used predominantly for acid gas removal.

The novel concept behind the IFPEXOL-1 process is to use a portion of the water-saturated inlet feed to recover the methanol from the aqueous portion of the low temperature separator. That approach has solved a major problem with methanol injection in large facilities, the methanol recovery via distillation. Beyond that simple discovery, the cold section of the process is remarkably similar to a basic methanol injection process. Modifications to the process include water washing the hydrocarbon liquid from the low temperature separator to enhance the methanol recovery.

The IFPEXOL-2 process for acid gas removal is similar to an amine-type process except for the operating temperatures. The absorber operates below -29°C (-20°F) to minimize methanol losses, and the regenerator operates at approximately 90 psi. Cooling is required on the regenerator condenser to recover the methanol. This process usually follows the IFPEXOL-1 process, so excessive hydrocarbon absorption is not as great a problem.

Methanol is probably one of the most versatile solvents for processing gas streams. Historically, methanol was the first commercial organic physical solvent and has been used for hydrate inhibition, gas dehydration, gas sweetening, and liquids recovery. Most of these applications involve low temperature where the physical properties of methanol are advantageous when compared to other solvents which exhibit high viscosity problems or even solids formation. Operation at low temperatures tends to suppress methanol's most significant disadvantage, high solvent loss. Methanol shows both polar and non-polar characteristics, and these characteristics give methanol the unique ability to be used in an extensive range of applications.

See also: Gas Cleaning.

IFP Spent Tire Depolymerization Process

A relatively new approach to the decomposition of used tires is the IFP process developed by the French Institute of Petroleum. Unlike the other tire pyrolysis processes, the IFP process is different in that it is a batch process that does not require pretreatment of the scrap tire.

In the process, whole tires are placed in a basket and lowered into the reactor where hot oil at 380°C (715°F) is sprinkled on to the surface of the tire. A chemical reaction between the hot oil and tires causes the depolymerization of the rubber.

After the tires have been completely depolymerized, the reactor is cooled to 100°C (212°F). The off-gases are sent to a distillation column. The column separates the gas and low-boiling hydrocarbon fractions. The resultant gas is sent for further purification into a C₄-C₆ fraction and gasoline constituents (C₈-C₁₀), and the low-boiling hydrocarbon derivatives are recycled to the reactor. The recycled hydrocarbon fraction is used to dilute the viscous fuel oil generated during the depolymerization process. Upon evacuating the reactor, the scrap metal is removed and sent off-site for salvage.

Since the process is operated in a batch mode, the concern over having enough tires for continuous feed is eliminated.

See also: Tires – Scrap.

Ignifluid Combustion System

In the Ignifluid system, an air-blown fluidized bed of coarse particles of the fuel generates a low heat content fuel gas, which is burned in secondary combustion within the free space above the fluidized bed.

Combustion of carbonaceous feedstocks in a high-temperature fluidized bed with clinker formation was developed as the Ignifluid boiler. In fluidized-bed combustion, the fuel is dispersed and burnt in a fluidized bed of inert particles. The amount of fuel that can be burnt in a fluidized bed is determined by the air-supply rate. In fluidized combustion, the fuel is burnt within a fluidized bed of mineral matter coal ash, silica sand, or limestone for sulfur retention. The passage of the air for combustion through the bed maintains the particles in a violently fluidized state. Interest in combustion of oil in fluidized beds is a result of their capability of burning the entire range of fuel oils from gas oil to vacuum residues and of reducing the emission of sulfur dioxide by addition of limestone. Boilers for industrial steam raising or heating, of either the water tube or shell type, can be fired by fluidized combustion.

The Ignifluid fuel-burning system consists of an inclined chain-grate stoker with combustion air supplied at high velocity (approximately 50 feet/second) through the stoker bars at which the crushed carbonaceous feedstock, at the upper end of the chain-grate stoker, is blown off the grates and burns in suspension. The larger feedstock particles recirculate in the space above the grates until burning is complete. Ash is agglomerated into spheres approximately 1.0 inch in diameter, some of which may remain in the space between the furnace walls and the chain grate to provide a sloping sidewall to redirect recirculating particles of feedstock into the combustion zone. The ash is eventually conveyed, by the moving stoker gates, to an ash pit.

See also: Combustion, Fluid Bed.

Ignitability

Ignitability is a property that is characteristic of liquids whose vapors are likely to ignite in the presence of ignition source; also characteristic of non-liquids that may catch fire from friction or contact with water and that burn vigorously. Also, here are three types of ignitable forms: (i) liquids with a flash point—the lowest temperature at which fumes above waste ignite of 60°C (140°F) which include alcohol, gasoline, and acetone, (ii) solids that spontaneously combust, and (iii) oxidizers and compressed gasses.

The ignitability properties of exposed material depends on: (i) the heat supplied, (ii) the exposure time, (iii) the presence or absence of flames, (iv) the rate of heat release, (v) the rate of flame spread, and (vi) the gas temperature.

See also: Hazardous Waste.

Ignitable Liquid

An ignitable liquid is a liquid that has a flash point of less than 60°C (140°F). Examples are benzene, hexane, heptane, benzene, pentane, petroleum ether (low boiling), toluene, and xylene(s). An aqueous solution that has a pH of less than or equal to 2, or greater than or equal to 12.5 is considered *corrosive*.

Corrosive materials also include substances such as sodium hydroxide and some other acids or bases. Chemicals that react violently with air or water are considered reactive. Examples are sodium metal, potassium metal, phosphorus, etc. Reactive materials also include strong oxidizers such as perchloric acid (HClO_4), and chemicals capable of detonation when subjected to an initiating source, such as solid, dry ($<10\% \text{H}_2\text{O}$) picric acid, benzoyl peroxide, or sodium borohydride (NaBH_4). Solutions of certain cyanide or sulfides that could generate toxic gases are also classified as reactive.

Immiscibility

Immiscibility is the formation of separate phases, the formation of carbonaceous solids, the separation of waxy materials, the separation of asphaltene constituents, an increase in viscosity of the material during storage, and the precipitation of oxidized or polymerized products. Immiscibility occurs when two or more fluids that do not have complete mutual solubility and co-exist as separate phases.

Residual fuel oils are produced by the blending of residual products with a diluent such as middle distillate to produce the grade of fuel oil required. This provides untold pathways, both chemical and physical, for problems such as immiscibility when these streams are mixed. For example, when vacuum residua serve as fuel oil stock rather than as a feedstock for visbreaking, it must be blended with other feed streams; immiscibility can and often does occur, especially if a blending stock does not contain sufficient aromatic content to solubilize the high asphaltene content of the vacuum residue.

See also: Immiscibility – Test Methods, Incompatibility.

Immiscibility – Test Methods

There are several test protocols that give a degree of the potential incompatibility tendencies of a fuel. The compatibility spot test (ASTM D4740) is one of these procedures. In brief, a drop of preheated fuel is thermally stressed at 100°C (212°F) for one hour and the spot examined for solids formation. Fuel blends are treated the same, each fuel separately and then the blend.

A second procedure (ASTM D2781) gives a compatibility rating based on how far a fuel and the blend spread on a specific brand of chromatographic paper. The rating scale is based on whether the spot gives a homogeneous (in terms of color) spot or a heterogeneous spot of light and dark areas.

A third procedure is known as the xylene equivalent test and is also a spot test on chromatographic paper. It differs from the other spot tests in that it used the percentage of xylene and iso-octane solvent that is required to be added to the fuel blend to give a homogeneous spot. Finally, a hot filtration test is used for an estimate of the potential for sludge formation.

See also: Immiscibility.

Impulse Turbines

Impulse turbines or turbine stages are simple, single-rotor or multirotor (compounded) turbines to which impulse blades are attached. Impulse blades can be recognized by their shape. Because they are usually used in the entrance high-pressure stages of a steam turbine, when the specific volume of steam is low and requires much smaller flow areas than at lower pressures, the impulse blades are short and have constant cross sections. Impulse turbines are also characterized by the fact that most or all of the enthalpy and hence the pressure drop occurs in the nozzles (or fixed blades that act as nozzles) and little or none in the moving blades. In the impulse turbine, no pressure drop (except that caused by friction) occurs in the moving blades.

A reaction turbine is a turbine that is constructed of rows of fixed and rows of moving blades, and the blades act as nozzles. The moving blades move as a result of the impulse of steam received (caused by change in momentum) and also as a result of expansion and acceleration of the steam relative to them, and they also act as nozzles. The enthalpy

drop per stage of one row fixed and one row moving blades is divided among them, often equally. Thus a blade with a 50% degree of reaction, or a 50% reaction stage, is one in which half the enthalpy drop of the stage occurs in the fixed blades and half in the moving blades. The pressure drops will not be equal, however. They are greater for the fixed blades and greater for the high pressure.

The single-stage impulse turbine (also called the de Laval turbine) consists of a single rotor to which impulse blades are attached. The steam is fed through one or several convergent-divergent nozzles which do not extend completely around the circumference of the rotor, so that only part the blades are impinged upon by the steam at any one time.

The velocity-compounded turbine was first proposed to solve the problems of a single-stage impulse turbine for use with high pressure and high temperature steam. The Curtis stage turbine, as it came to be called, is composed of one stage of nozzles as the single-stage turbine, followed by two rows of moving blades instead of one. These two rows are separated by one row of fixed blades attached to the turbine stator, which has the function of redirecting the steam leaving the first row of moving blades to the second row of moving blades.

Incinerator

An incinerator is a device used to burn solid or liquid residues or wastes as a method of disposal.

The incinerator is, simply, a furnace for burning refuse, and modern incinerators include pollution mitigation equipment such as flue-gas cleaning. There are various types of incinerator plant design which include (i) simple incinerator, (ii) fixed or moving grate incinerator, (iii) rotary-kiln incinerator, and (iv) the fluidized bed incinerator.

The simple incinerator is an older and simpler kind of incinerator that is, essentially, a brick-lined cell with a metal grate over a lower ash pit, with one opening in the top or side for loading and another opening in the side for removing incombustible solids clinker. Many small incinerators formerly found in apartment houses have now been replaced by waste compactors.

The fixed or moving grate incinerator is a large, fixed hearth incinerator with a moving grate. The moving grate enables the movement of waste through the combustion chamber to be optimized to allow a more efficient and complete combustion. These incinerators are typically used for combustion of municipal waste, and are thus referred to as MSWIs (municipal solid waste incinerators).

In the fixed or moving grate incinerator, the waste is introduced by a waste crane through the “throat” at one end of the grate, from where it moves down over the descending grate to the ash pit in the other end. Here, the ash is removed through a water lock. Part of the combustion air (primary combustion air) is supplied through the grate from below. This air flow also has the purpose of cooling the grate itself. Cooling is important for the mechanical strength of the grate, and many moving grates are also water cooled internally. Secondary combustion air is supplied into the boiler at high speed through nozzles over the grate. It facilitates complete combustion of the flue gases by introducing turbulence for better mixing and by ensuring a surplus of oxygen.

The incinerator must be designed to ensure that the flue gas reaches a temperature of at least 850°C (1,560°F) in order to ensure proper breakdown of organic toxins. This includes backup auxiliary burners (often fueled by oil), which are fired into the boiler in case the heating value of the waste becomes too low to reach this temperature alone. The flue gases are then cooled by heat transfer and heat the steam to typically 400°C (750°F) at a pressure of 550 to 600 psi for the electricity generation in the turbine. At this point, the flue gas has a temperature of around 200°C, and is passed to the flue gas cleaning system.

The rotary kiln incinerator has a primary chamber and secondary chamber. The primary chamber consists of an inclined refractory lined cylindrical tube. Movement of the cylinder on its axis facilitates movement of waste. In the primary chamber, there is conversion of solid fraction to gases, through volatilization, destructive distillation and partial combustion reactions. The secondary chamber is necessary to complete gas phase combustion reactions.

The clinker spills out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases may be combusted in an afterburner. To control air pollution, the combustion product gases are further treated with acid gas scrubbers to remove sulfuric acid and nitric acid emissions, and then routed through bag houses to remove particulate matter before the gases are released into the atmosphere.

The fluidized bed incinerator uses a strong airflow through a sand bed until a point is reached where the sand particles separate to let the air through and mixing and churning occurs, thus a fluidized bed is created and fuel and waste can now be introduced. The sand with the pre-treated waste and/or fuel is kept suspended on pumped air currents and takes on a fluid-like character. The bed is thereby thoroughly mixed and agitated keeping small inert particles and air in a fluid-like state. This allows all of the mass of waste, fuel, and sand to be fully circulated through the furnace.

The heat produced by an incinerator can be used to generate steam which may then be used to drive a turbine in order to produce electricity. However, the amount of energy produced is very much dependent upon the type and composition of the waste used as the feedstock. Much of the current thinking involves co-incineration of a specified amount of the waste (calculated on the basis of the carbon content of the waste) with, for example, coal to produce a consistent amount of energy.

Incineration has a number of outputs such as the ash and the emission to the atmosphere of flue gas. Before the flue gas cleaning, the flue gases may contain significant amounts of particulate matter, heavy metals, dioxins, furans, sulfur dioxide, hydrochloric acid, and polynuclear aromatic hydrocarbon derivatives (carcinogens).

The most publicized concerns related to the incineration of municipal solid wastes involve the fear that it produces significant amounts of dioxin and furan emissions. Dioxins and furans are considered by many to be serious health hazards. Older-generation incinerators that were not equipped with modern gas cleaning technologies were indeed significant sources of dioxin emissions. However, modern incinerators (due to advances in emission control designs and stringent regulations) must limit and even mitigate such emissions.

Particulate matter is collected by particle filtration, most often electrostatic precipitators and/or baghouse filters. Hydrogen chloride and sulfur dioxide are removed in scrubbers or as dry desulfurization by injection limestone slurry into the flue gas before the particle filtration. Wastewater from scrubbers must subsequently pass through a wastewater treatment plant. Nitrogen oxide (NO_x) emissions are either reduced by catalytic reduction with ammonia in a catalytic converter (selective catalytic reduction) or by a high temperature reaction with ammonia in the furnace (selective non-catalytic reduction). Heavy metals are often adsorbed on injected active carbon powder, which is collected by the particle filtration.

Incineration produces fly ash and bottom ash just as is the case when coal is combusted. The total amount of ash produced by municipal solid waste incineration ranges from 15 to 20% by weight of the waste, and the fly ash amounts to 0 to 10% of the total ash. The fly ash, by far, constitutes more of a potential health hazard than does the bottom ash because the fly ash often contains high concentrations of heavy metals such as lead, cadmium, copper, and zinc as well as small amounts of dioxins and furans. The bottom ash seldom contains significant levels of heavy metals.

While fly ash is always regarded as hazardous waste, bottom ash is generally considered safe for regular landfill after a certain level of testing defined by the local legislation. Ash, which is considered hazardous, may generally only be disposed of in landfills which are carefully designed to prevent pollutants in the ash from leaching into underground aquifers – or after chemical treatment to reduce its leaching characteristics.

See also: Combustion.

Inclined Grate Furnace

The inclined grate furnace (moving grate furnace, step grate furnace) is a type of furnace in which fuel enters at the top part of a grate in a continuous ribbon, passes over the upper drying section where moisture is removed, and descends into the lower burning section. Ash falls off the lower end of the grate, and is readily removed mechanically. This type of furnace is extremely versatile (in terms of flexibility of the ability to tolerate different types of fuel).

In the system, biomass fuel (for example wood) is delivered to the top of a sloping grate by auger (Figure 1) or by a ram-stoker and lock-hopper. This grate is constructed of several panels of firebars. Electric or hydraulic actuation moves these bars in sequence to encourage fuel to travel down the grate.

Primary air is supplied under the grate, and the fuel passes through a clear sequence of drying, volatile emission, and char burnout as it moves down the grate. This sequenced combustion is one of the great strengths of the design: by tuning the grate speed, fuel feed, and air supply, it is possible to burn a wide range of fuels. The addition of a

ceramic arch over the grate reflects heat back, encouraging drying and subsequent ignition, and thus permitting the combustion of wet fuels: up to 70% moisture has been achieved.

The furnace has a wide tolerance of fuel type, moisture, and particle size, and the positive movement of fuel down grate avoids clinkering and blockages. The furnace also has a high efficiency.

On the other hand, a relatively large fuel inventory can lead to slow response to load swings, although modulating controls using a lambda sensor and air trim improve this controllability. The furnace is often more expensive than other types of furnace.

See also: Biomass, Combustion.

Incompatibility

Incompatibility is the immiscibility of crude oil products and also of different crude oils which is often reflected in the formation of a separate phase after mixing and/or storage.

The incompatibility of liquid fuels has become a major issue over the past two decades as a result of the production of fuels from sources other than crude oil. Differences in fuel composition and in the chemical nature of the fuel constituents have all served to emphasize the issue of fuel incompatibility.

Briefly, incompatibility refers to the formation of a precipitate (or sediment) or phase separation when two liquids are mixed. The term instability is often used in reference to the formation of color, sediment, or gum in the liquid over a period of time. This term may be used in contrast to the formation of a precipitate in the near, almost immediate term. However, the terms are often used interchangeably. Gum formation alludes to the formation of soluble organic (usually considered to be polymeric) material, whereas sediment is considered to be insoluble organic (usually polymeric) material.

In general, fuel instability and incompatibility can be related to the existence of heteroatoms (i.e., containing nitrogen, oxygen, and sulfur). The degree of unsaturation of the fuel (i.e., the level of olefinic species) also plays a role in determining instability/incompatibility. Also, recent investigations have implicated catalytic levels of various oxidized intermediates and acids as especially deleterious for middle distillate fuels.

Fuel incompatibility can have many meanings. The most obvious example of incompatibility (immiscibility) is the inability of a hydrocarbon fuel and water to mix. In the present context, incompatibility usually refers to the presence of various polar functionalities (i.e., heteroatom function groups containing nitrogen, oxygen, or sulfur, and even various combinations of the heteroatoms) in the crude oil. As is often the case, some of the polar functional groups can survive the refining operations (perhaps with some change) and end up in the finished fuel products. Thereafter, the groups can participate in a variety of chemical reactions, leading to fuel deterioration and/or instability and incompatibility.

Fuel instability problems can be of two related types: high-temperature short-term reactions (oxidative instability) and ambient temperature long-term reactions (storage instability). Oxygen, nitrogen, and sulfur species can be implicated in both types of instability. The synergism between organic sulfur and nitrogen compounds with active oxygen species on the stability of middle distillate fuels is not well understood. Differences in fuel composition, reaction surface, quantity of dissolved oxygen, hydroperoxide concentration, and reaction temperature all contribute to the reported variations in fuel deterioration.

Both incompatibility and instability result in the formation and separation of degradation products or in other undesirable changes in the original properties of petroleum products. In the case of instability, there is a low resistance of the product to environmental influences during storage or to its susceptibility to oxidative or other degradation processes. In the case of incompatibility, degradation products form or changes occur due to an interaction of some chemical groups present in the components of the final blend.

To summarize, part of the problem of incompatibility arises from the manner in which the fuels react with oxygen during storage. The remainder of the problem may be due to the character of the individual constituents. Many of the constituents may be incompatible/immiscible with each other, thereby causing phase separation and hence, incompatibility. Another part of the problem (not to be underestimated) arises because of variations in terminology. The nonspecific application of various names is confusing and needs to be resolved.

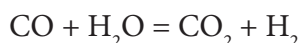
See also: Immiscibility, Immiscibility – Test Methods, Instability and Incompatibility – Methods for Determining.

Indirect Liquefaction

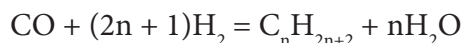
Indirect liquefaction is the conversion of biomass to a liquid fuel through an intermediate step involving gasification of the feedstock to synthesis gas followed by the production of hydrocarbon liquids from the gas.

Thus, indirect liquefaction processes invoke the concept of a two-stage conversion operation in which the feedstock is first converted (by reaction with steam and oxygen) to produce a gaseous mixture that is composed primarily of carbon monoxide and hydrogen (synthesis gas; syn gas). The gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products.

The gasification step may be attained by means of any one of several processes. The exothermic nature of the process and the decrease in the total gas volume in going from reactants to products suggest the most suitable experimental conditions to use in order to maximize product yields. In practice, the Fischer-Tropsch reaction is carried out at temperatures on the order of 200 to 350°C (390 to 660°F) and at pressures up to 4,000 psi. The hydrogen/carbon monoxide ratio is usually at approximately 2.2:1 or 2.5:1. Since up to three volumes of hydrogen may be required to achieve the next stage of the liquids production, the synthesis gas must then be converted by means of the water-gas shift reaction) to the desired level of hydrogen:



After which the gaseous mix is purified (acid gas removal, etc.) and converted to a wide variety of hydrocarbon derivatives:



These reactions result primarily in low- and medium-boiling aliphatic compounds; present commercial objectives are focused on the conditions that result in the production of n-hydrocarbon derivatives as well as olefinic and oxygenated materials.

The efficiency of a two-stage process as compared with a single-stage liquefaction process (such as pyrolysis of biomass to bio-oil) is a disadvantage of the indirect liquefaction process, but the advantages of the indirect approach are (i) the gasification stage can tolerate a higher degree of impurities (such as mineral matter) in the feedstock, (ii) the feedstock to the liquefaction stage can be maintained at the desired hydrogen level irrespective of the nature and quality of the feedstock, (iii) a clean product is produced, and (iv) hydrogen from a variety of other hydrogen production methods may be employed thereby increasing the overall production of liquids from a given amount of biomass or waste.

See also: Synthesis Gas.

Indirect Liquefaction Processes

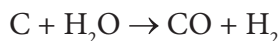
The indirect liquefaction of a carbonaceous feedstock involves a two-stage conversion operation in which the feedstock is first converted (by reaction with steam and oxygen) to produce a gaseous mixture that is composed primarily of carbon monoxide and hydrogen (syngas; synthesis gas). The gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products.

In addition to the production of fuel gas, the feedstock may be gasified to prepare synthesis gas (carbon monoxide, CO, and hydrogen, H₂), which may be used to produce a variety of products, including ammonia, methanol, and liquid hydrocarbon fuels.

The synthesis of hydrocarbon derivatives from carbon monoxide and hydrogen (synthesis gas) (the Fischer-Tropsch synthesis) is a procedure for the indirect liquefaction of coal. This process is the only coal liquefaction scheme currently in use on a relatively large commercial scale; South Africa is currently using the Fischer-Tropsch

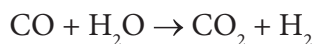
process on a commercial scale in their SASOL complex, although Germany produced roughly 156 million barrels of synthetic crude oil annually using the Fischer-Tropsch process during the Second World War.

Thus, the indirect liquefaction of coal involves (as a first stage) the production of a synthesis gas mixture from the coal followed by the catalytic formation of hydrocarbon derivatives and oxygenated species from the synthesis gas. In the process, the feedstock is converted to gaseous products at temperatures in excess of 800°C (1,470°F), and at moderate pressures, to produce synthesis gas:

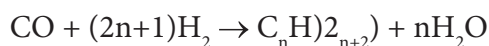


The gasification may be attained by means of any one of several processes, and the exothermic nature of the process and the decrease in the total gas volume in going from reactants to products suggest the most suitable experimental conditions to use in order to maximize product yields. The process should be favored by high pressure and relatively low reaction temperature. In practice, the Fischer-Tropsch reaction is carried out at room temperatures of 200 to 350°C (390 to 660°F) and at pressures of 75 to 4,000 psi; the hydrogen/carbon monoxide ratio is usually at approximately 2.2:1 or 2.5:1.

Since up to three volumes of hydrogen may be required to achieve the next stage of the liquids production, the synthesis gas must then be converted by means of the water-gas shift reaction) to the desired level of hydrogen:



After which the gaseous mix is purified (acid gas removal, etc.) and converted to a wide variety of hydrocarbon derivatives:



These reactions result primarily in low- and medium-boiling aliphatic compounds; present commercial objectives are focused on the conditions that result in the production of n-hydrocarbon derivatives as well as olefins and oxygenated materials.

Although the efficiency of a two-stage process as compared with a single-stage liquefaction process has often been cited as a disadvantage of the indirect liquefaction of coal, the advantages of the indirect approach are (i) the gasification stage can tolerate a higher degree of impurities (e.g., mineral matter) in the coal; (ii) the feed to the liquefaction stage can be maintained at the desired hydrogen level irrespective of the nature and quality of the feed coal; (iii) a clean product is produced; (iv) the method is adaptable to the use of the products from the underground gasification of coal; and (v) there is the added advantage that hydrogen from a variety of other hydrogen production methods may be employed thereby increasing the overall production of liquids from a given amount of coal.

Indirectly Heated Gasifiers

The fluidizing media for the biomass gasification are either air and steam or pure oxygen and steam. Air-blown or directly heated gasifiers use the exothermic reaction between the oxygen and organics to provide the heat necessary to devolatilize biomass and to convert residual carbon-rich chars. For directly heated gasifiers, the heat to drive the process is generated inside within the gasifier. When air is used, the product gas is diluted with nitrogen and typically has a dry basis calorific value of 110 to 160 Btu/ft³. The use of oxygen instead of air produces a medium heating value syngas, 265 to 400 Btu/ft³, suitable for combustion turbine application.

Oxygen production is expensive, and hence indirectly heated gasifiers which utilize the twin bed concept similar to fluid catalytic crackers (FCC) that are being used in refining crude oil are being developed for generation of medium calorific syngas using air as a fluidizing medium.

The syngas produced from the indirectly heated gasifiers are devoid of nitrogen contamination, and hence they are also favored for other gas-to-liquid-based technologies. The non-requirement of oxygen to generate medium heating value syngas, results in lower capital cost for the gasification plant.

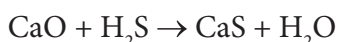
If the gas turbines using fossil fuel (natural gas or diesel) which has heating value of approximately 885 Btu/ft³, need to be interchangeable with the biomass syngas, higher heating values are preferred. In a natural-gas-fired turbine, the gas is only approximately 2% of the flow and the rest is air for dilution and combustion, while in contrast, syngas accounts for 14 to 16% v/v of the total gas.

The IGCC (Integrated Gasification Combined Cycle) uses air as the gasifying agent and require modified turbine combustors to handle the low heating-value gas (110 to 190 Btu/ft³). The low calorific syngas up to 135 Btu/ft³ is only suitable for firing in the boiler or use in diesel engines.

The COGAS char gasifier (Figure 1) is an indirectly heated unit that has been developed for use in combination with a pyrolysis process to gasify the residual char remaining after pyrolysis.

The COGAS process typifies how a circulating heat transfer medium, in this case char, can be heated and then reintroduced into the gasifier to provide the required heat without diluting the product gas with nitrogen and without the need to produce pure oxygen.

In some indirectly heated systems, the heat transfer medium is selected to serve secondary functions that improve the overall gasifier performance. For example, in the CO₂ Acceptor process (Figure 2), lime (CaO) or dolomite (CaO-MgO) is used to chemically trap the hydrogen sulfide:



Much of the heat required is supplied by the highly exothermic reaction of the dolomite and carbon dioxide, rather than by the sensible heat of the heat transfer medium, as in the case of the COGAS gasifier. Removal of carbon dioxide and hydrogen sulfide from the synthesis gas directly in the gasifier has several important advantages.

The acceptor contains some 80 to 90% of the sulfur in the lignite, but only approximately 10% of this is driven off in the regenerator. The regenerator flue gas contains sulfur dioxide, and requires scrubbing before being released to the atmosphere.

See also: Gasification, Gasification of Biomass.

Industrial Chemicals

Industrial chemicals are used widely in all kinds of industries. Although the use of these chemicals has played a major role in the development of industry and society in the past few decades, most current pollution problems are becoming more serious due to the ubiquitous industrial chemicals in the environment.

Industrial chemicals are released by volatilization, leakage, or leaching, either during the lifetime of a product or after ultimate disposal. Although not all of these constitute potential toxicity hazards, many will cause environmental pollution as a result of leakage during storage, from use in the environment or from their disposal—either directly, or of wastes containing them. Apart from industrial uses, a large number of chemicals are used in domestic products and so their use and disposal are less controlled than that of industrial chemicals. For example, industrial chemicals such as food additives, surfactants, and medicines are used directly in human life.

Although industrial chemicals play an important role in improving human health and standard of living, they have caused significant problems to the no-linger pristine environment. These anthropogenic contaminants include inorganic compounds, organic substances, heavy metals, and radionuclides. A health problem is posed whenever people become exposed to them, even at low concentrations.

Some industrial chemicals, particularly persistent organic pollutants, which occur in the environment are both highly toxic and difficult to remove. Moreover, industrial chemicals also include endocrine-disrupting chemicals that cause adverse health effects in an intact organism, or its progeny, as a result of changes in endocrine function. All of these compounds can cause adverse effects on human health and damage ecosystems. As

these chemicals in the environment cause great potential risk, great attention should be paid to recognizing them.

Organic chemicals are some of the important starting materials for a great number of major fuels industries and chemical industries. The production of organic chemicals as raw materials or reagents for other applications is a major sector of manufacturing polymers, pharmaceuticals, pesticides, paints, artificial fibers, food additives, etc. Organic synthesis on a large scale, compared to the laboratory scale, involves the use of energy, basic chemical ingredients from the petrochemical sector, catalysts, and after the end of the reaction, separation, purification, storage, packaging, distribution, etc. During these processes, there are many problems of health and safety for workers in addition to the environmental problems caused by their use and disposition as waste.

The industrial organic chemical industry uses feedstocks derived from natural gas and crude oil (approximately 90%), recovered coal tar condensates generated by coke production (approximately 10%) as well as from renewable sources such as the biomass industry.

The chemicals industry is diverse, comprising (i) basic or commodity chemicals, (ii) specialty chemicals derived from basic chemicals, such as adhesives and sealants, catalysts, coatings, electronic chemicals, and plastic additives, (iii) products derived from life sciences, such as pharmaceuticals, pesticides and products of modern biotechnology, and (iv) consumer care products, such as soap, detergents, bleaches, hair and skin care products, and fragrances.

The chemical industry involves the use of chemical processes such as chemical reactions and refining methods to produce a wide variety of solid, liquid, and gaseous materials. Most of these products serve to manufacture other items, although a smaller number go directly to consumers. Solvents, pesticides, lye, washing soda, and Portland cement provide a few examples of product used by consumers. The industry includes manufacturers of organic-industrial chemicals, petrochemicals, agrochemicals, polymers and rubber (elastomers), oleo-chemicals (oils, fats, and waxes), explosives, fragrances, and flavors.

Chemical processes such as chemical reactions operate in chemical plants to form new substances in various types of reaction vessels. In many cases, the reactions take place in special corrosion-resistant equipment at elevated temperatures and pressures with the use of catalysts. The products of these reactions are separated using a variety of techniques including distillation, especially fractional distillation, precipitation, crystallization, adsorption, filtration, sublimation, and drying.

The processes and product or products are usually tested during and after manufacture by dedicated instruments and on-site quality control laboratories to ensure safe operation and to assure that the product will meet required specifications. More organizations within the industry are implementing chemical compliance software to maintain quality products and manufacturing standards. The products are packaged and delivered by many methods, including pipelines, tank-cars, and tank-trucks (for both solids and liquids), cylinders, drums, bottles, and boxes. Chemical companies often have a research-and-development laboratory for developing and testing products and processes. These facilities may include pilot plants, and such research facilities may be located at a site separate from the production plant(s).

Industrial organic chemical manufacturers use and generate both large numbers and quantities of chemicals. The types of pollutants a single facility will release depend on the feedstocks, processes, equipment in use, and maintenance practices. These can vary over a short period of time (sometimes on an hour-to-hour basis) and can also vary with the part of the process that is underway. For example, for batch reactions in a closed vessel, the chemicals are more likely to be emitted at the beginning and end of a reaction step (associated with vessel loading and product transfer operations), than during the reaction.

Industrial organic synthesis followed a largely *stoichiometric* line of evolution that can be traced back to the synthesis of mauveine by Perkin, the subsequent development of the dyestuffs industry based on coal tar, and the fine chemicals and pharmaceuticals industries, which can be regarded as spin-offs from the dyestuffs industry. Consequently, fine chemicals and pharmaceuticals manufacture, which is largely the domain of synthetic organic chemists, is rampant with classical stoichiometric processes.

The desperate need for more catalytic methodologies in industrial organic synthesis is nowhere more apparent than in oxidation chemistry. For example, as any organic chemistry textbook will note that the reagent of choice for the oxidation of secondary alcohols to the corresponding ketones, a pivotal reaction in organic

synthesis, is the Jones reagent. The latter consists of chromium trioxide and sulfuric acid and is reminiscent of the phloroglucinol process referred to earlier. The introduction of the storage-stable pyridinium chlorochromate (PCC) and pyridinium dichromate (PDC) in the 1970s, represented a practical improvement, but the stoichiometric amounts of carcinogenic chromium(VI) remain a serious problem. Obviously, there is a definite need in the fine chemical and pharmaceutical industry for catalytic systems that are green and scalable and have broad utility.

Industrial Waste

Waste is the remains or by-product from a process for which no use is planned or foreseen. The words domestic (or municipal) and industrial are qualifiers of the source of the waste and, to some extent, also descriptive of the contents of the waste. Once a material has been designated as waste, it remains waste until it has been fully recovered and no longer poses a potential threat to the environment.

Industrial waste is a waste type produced by industrial operations, such as factories, mines, and refineries. Toxic waste and chemical waste are two more specific designations of industrial waste.

Industrial process wastes include a very wide range of materials, and the actual composition of industrial wastes in a country will depend on the nature of the industry. Wastes may occur as relatively pure substances or as complex mixtures of varying composition and in varying physicochemical states. Examples of the materials which may be found under this heading are general rubbish, organic wastes from food processing, acids, alkalis, metallic sludge, and tar. The most important feature of industrial wastes is that a significant proportion is regarded as hazardous or potentially toxic, thus requiring special handling, treatment, and disposal.

The energy content of waste can be harnessed directly by using the waste as a direct combustion fuel, or indirectly by processing them into another type of fuel. Recycling through thermal treatment ranges from using waste as a fuel source for cooking or heating, to fuel for boilers to generate steam and electricity in a turbine.

Pyrolysis and gasification are two related forms of thermal treatment where waste materials are heated to high temperatures with limited oxygen availability. The process usually occurs in a sealed vessel under high pressure.

Pyrolysis of solid waste converts the material into solid, liquid, and gas products. The liquid and gas can be burnt to produce energy or refined into other products. The solid residue (char) can be further refined into products such as activated carbon.

Gasification and advanced plasma arc gasification are used to convert organic materials directly into a synthetic gas (syngas) composed of carbon monoxide and hydrogen. The gas is then burnt to produce electricity and steam.

See also: Combustion, Gasification, Waste.

Inertial Separator

An inertial separator separates particulate matter or dust from gas streams using a combination of forces, such as centrifugal, gravitational, and inertial. These forces move the dust to an area where the forces exerted by the gas stream are minimal. The separated dust is moved by gravity into a hopper, where it is temporarily stored.

The three primary types of inertial separators are (i) settling chambers, (ii) baffle chambers, and (iii) centrifugal collectors. Neither settling chambers nor baffle chambers are commonly used in the minerals processing industry. However, their principles of operation are often incorporated into the design of more efficient dust collectors.

In gas processing, the gas passes through an inlet baffle to remove large liquid droplets, and then through a series of angled vanes that impart inertial forces on the smaller liquid droplets.

See also: Gas Cleaning.

Inferred Reserves

The term inferred reserves is also commonly used in addition to, or in place of, potential reserves (Table I-1).

Table I-1 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Inferred reserves are regarded as of a higher degree of accuracy than potential reserves, and the term is applied to those reserves that are estimated using an improved understanding of reservoir frameworks. The term also usually includes those reserves that can be recovered by further development of recovery technologies.

The differences between the data obtained from these various estimates can be considerable, but it must be remembered that any data related to the reserves of crude oil (and, for that matter, related to any other fuel or mineral resource) will always be open to questions related to the degree of certainty. Thus, in reality, and in spite of the use of self-righteous word-smithing, proven reserves may be a small part of the total hypothetical and/or speculative amounts of a resource.

Inherent Mineral Matter

Inherent mineral matter is the mineral matter which had its origin in the organic constituents of the plant but the extraneous mineral matter was brought into the plant by mechanical means from outside, for example, as dust by air or as suspended or dissolved material carried by water. The inherent mineral matter is also sometimes defined as the inorganic material combined with the organic coal substance, but such material need not be derived from the coal-forming plants.

Inherent mineral matter is usually much smaller in quantity than extraneous mineral matter and can be expected to differ quite markedly in composition from the inorganic residue of the major plant types. This is due to re-use (in no small part) of the inorganic elements by succeeding vegetation and to leaching of inorganic constituents by the waters percolating and flowing through the area during growth of the plants. The percolating waters may be presumed to have an increased dissolving action on the inorganic constituents because of their content of humic acids, carbon dioxide, and other products of decay. Furthermore, the differences in solubilities and reactions of the inorganic elements present in the plants dictate that these elements do not contribute to the mineral matter in proportion to their presence in the plant material.

See also: Clay Minerals, Minerals.

Inorganic Chemicals

Inorganic chemistry is the branch of chemistry concerned with the properties and behavior of inorganic compounds. This field covers all chemical compounds except the myriad of carbon-based compounds (such as the hydrocarbon derivatives), which are the subjects of organic chemistry. The distinction between the two disciplines is far from absolute, and there is much overlap, most importantly in the sub-discipline of organometallic chemistry in which

organic compounds and metals from distinct and stable products. An example is tetraethyl lead which was formerly used in gasoline (until it was banned by various national environmental agencies) as an octane enhancer to prevent engine knocking or pinging during operation.

The term inorganic chemicals represents a broad class of substances encompassing all those chemicals that do not include carbon and its derivatives as their principal elements. The exceptions (alphabetically) are (i) carbide derivatives, which are compounds composed of carbon and less electronegative elements and are distinguished by the chemical bonding – ionic, covalent – which are generally prepared from metals or metal oxides at high temperatures (1,500°C, 2,730°F, or higher) by combining the metal with carbon, (ii) carbonate derivatives, which are salts of carbonic acid, H_2CO_3 , and characterized by the presence of the carbonate ion, a polyatomic ion with the formula of CO_3^{2-} , (iii) cyanate derivatives, which contain the cyanate anion ($\text{O}=\text{C}=\text{N}^-$), usually written OCN^- , – cyanate derivatives are also isomers of the much less stable fulminate anion $[\text{C}\equiv\text{N}^+\text{O}]^-$, and (iv) cyanide derivatives, which are chemical compounds that contain the group $\text{C}\equiv\text{N}$ that, in inorganic chemicals consists of a carbon atom triple-bonded to a nitrogen atom and is present as the anion CN^- leading to salts such as sodium cyanide (NaCN) and potassium cyanide (KCN) that are highly toxic.

In summary, many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Examples of salts (which are ionic compounds) are magnesium chloride (MgCl_2) which consists of magnesium cations (Mg^{2+}) and chloride anions (Cl^-). In any salt, the proportions of the ions are such that the electric charges cancel out, so that the bulk compound is electrically neutral. Important classes of inorganic compounds are the oxides, the carbonates, the sulfates, and the halides. Many inorganic compounds are characterized by high melting points, ease of crystallization, and solubility – where some salts (such as sodium chloride, NaCl) are highly soluble in water; others (such as silica, silicon oxide, and SiO_2) are insoluble in water.

See also: Inorganic Matter; Minerals, Organic Chemicals.

Inorganic Chemical Transformation Reactions

The various chemical transformation processes, which influence the presence and the analysis of inorganic chemicals at a particular site, although often represented by simple (and convenient) chemical equations, can be complex, and the true nature of the chemical transformation process is difficult to elucidate. The extent of transformation is dependent on many factors including (i) the properties of the chemical, (ii) the geology of the site, (iii) the climatic conditions, such as temperature, oxygen levels, and moisture, (iv) the type of micro-organisms present at the site, and (v) any other environmental conditions that can influence the life-cycle of the chemical. In fact, the primary factor controlling the extent of chemical transformation is the molecular composition of the inorganic chemicals contaminant.

Any chemical change can easily be represented with the help of chemical equations which is a simple representation of a chemical reaction and which involves the molecular or atomic formulas of reactants and products. On the basis of cleavage and formation of chemical bonds, most inorganic chemical reactions can be classified into four broad categories: (i) acid-base reactions, (ii) combination reactions, (iii) decomposition reactions, (iv) single displacement reactions, and (v) double displacement reactions.

One other type of reaction that occurs with inorganic chemicals and with organic chemicals is a coagulation reaction – for convenience, it is included here but is equally applicable to inorganic chemicals and to organic chemicals.

In the chemical sense, aggregation (especially particle agglomeration) refers to formation of assemblages in a suspension and represents a mechanism leading to destabilization of colloidal systems. During this process, particles dispersed in the liquid phase stick to each other, and spontaneously form irregular particle clusters, flocs, or aggregates. This phenomenon is also referred to as coagulation or flocculation, and such a suspension is also called unstable – both physically and chemically. Particle aggregation can be induced by adding salts or another chemical referred to as a coagulant or flocculant.

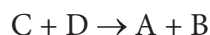
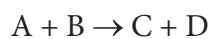
Particle aggregation is normally an irreversible process, and once particle aggregates have formed, they will not dissociate easily. In the course of aggregation, the aggregates will grow in size, and as a consequence, they may settle to the bottom of the container, which is referred to as sedimentation. Alternatively, a colloidal gel may form in concentrated suspensions which changes the rheological properties. The reverse process whereby particle aggregates

are disrupted and dispersed as individual particles, referred to as peptization, hardly occurs spontaneously, but may occur under stirring or shear. Colloidal particles may also remain dispersed in liquids for long periods of time (days to years). This phenomenon is referred to as colloidal stability, and such a suspension is said to be stable. In fact, stable suspensions are often obtained at low salt concentrations or by addition of chemicals referred to as stabilizers or stabilizing agents. Similar aggregation processes occur in other dispersed systems. For example, in an emulsion, they may also be coupled to droplet coalescence, and not only lead to sedimentation but also to creaming. In aerosols, airborne particles may equally aggregate and form larger clusters. In the chemical sense, creaming is the migration of the dispersed phase of an emulsion, under the influence of buoyancy. The particles float upwards or sink, depending on how large they are and how much less dense or more dense they may be than the continuous phase, and also how viscous or how thixotropic (a time-dependent shear thinning property) the continuous phase might be. For as long as the particles remain separated – the process is referred to as creaming.

Thus, a chemical transformation requires a chemical reaction to lead to the transformation of one chemical to another (Habashi, 1994). Typically, chemical reactions encompass changes that only involve the positions of electrons in the forming and breaking of chemical bonds between atoms, with no change to the nuclei (no change to the elements present), and can often be described by a relatively simple chemical equation; thus:



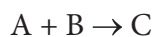
However, although the various chemical transformation processes that occur and which influence the presence and the analysis of inorganic chemicals at a particular site are often represented by simple (and convenient) chemical equations, the chemical transformation reactions can be much more complex than the equation indicates. In addition, a chemical reaction may proceed in the forward direction and processed to completion as well as in the reverse direction until the reactants and products reach an equilibrium state:



Thus,



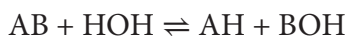
Reactions that proceed in the forward direction to approach equilibrium are often described as spontaneous, requiring no input of free energy to go forward. On the other hand, non-spontaneous reactions require input of free energy to go forward (examples application of heat for the reaction to proceed). In inorganic chemical synthesis, different chemical reactions are used in combinations during the reaction in order to obtain a desired product. Also, in inorganic chemistry, a consecutive series of chemical reactions (where the product of a reaction is the reactant of the next reaction) are often encouraged to proceed by a variety of catalysts which increase the rates of biochemical reactions without themselves (the catalysts) being consumed in the reaction, so that syntheses and decompositions impossible under ordinary conditions can occur at the temperatures, pressures, and reactant concentrations present within a reactor and, by inference, in the current content within the environment.



This simplified equation does not truly illustrate the potential complexity of an inorganic chemical reaction, but such complexity must be anticipated when an inorganic chemical is transformed in an environmental ecosystem. Actual examples (listed alphabetically) of the reaction of inorganic chemicals in the environment are presented in the following subsections.

Inorganic Chemical Transformation Reactions – Hydrolysis Reactions

Hydrolysis is a double decomposition reaction with water as a reactant. Thus, if an inorganic chemical is represented by the formula AB in which A and B are atoms or groups and water is represented by the formula HOH, the hydrolysis reaction may be represented by the reversible chemical equation:



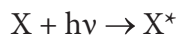
The reactants other than water, and the products of hydrolysis, may be neutral molecules (as in most hydrolysis reactions involving organic compounds) or ionic molecules (charged species), as in hydrolysis reactions of salts, acids, and bases.

In the reaction, the hydroxyl group replaces another chemical group on the inorganic molecule and hydrolysis reactions are usually catalyzed by hydrogen ions or hydroxyl ions. This produces the strong dependence on the acidity or alkalinity (pH) of the solution often observed but, in some cases, hydrolysis can occur in a neutral (pH = 7) environment. Adsorption on to a mineral sediment (such as a clay sediment that has strong adsorptive powers) generally reduces the rates of hydrolysis for acid- or base-catalyzed reactions. Neutral reactions appear to be unaffected by adsorption, although there is always the possibility that the mineral sediment can cause catalyzed chemical transformation reactions.

There are four possible general rules involving the reactions of salts in the aqueous environment: (i) if the salt is formed from a strong base and a strong acid, the salt solution is neutral, indicating that the bonds in the salt solution will not break apart (indicating no hydrolysis occurred) and is basic, (ii) if the salt is formed from a strong acid and weak base, the bonds in the salt solution will break apart and become acidic, (iii) if the salt is formed from a strong base and weak acid, the salt solution is basic and hydrolyzes, and (iv) if the salt is formed from a weak base and weak acid, it will hydrolyze but the acidity or basicity depends on the equilibrium constants of K_a and K_b . If the K_a value is greater than the K_b value, the resulting solution will be acidic and if the K_b value is greater than the K_a value, the resulting solution will be basic (Petrucchi et al., 2010).

Inorganic Chemical Transformation Reactions – Photolysis Reactions

Photolysis (also called photo-dissociation and photo-decomposition) is a chemical reaction in which an inorganic chemical (or an organic chemical) is broken down by photons and is the interaction of one or more photons with a target molecule. The photolysis reaction is not limited to the effects of visible light, but any photon with sufficient energy can cause the chemical transformation of the inorganic bonds of a chemical. Since the energy of a photon is inversely proportional to the wavelength, electromagnetic waves with the energy of visible light or higher, such as ultraviolet light, x-rays, and gamma rays, can also initiate photolysis reactions. The primary step of a photolysis reaction is:



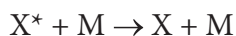
X^* : an electronically excited state of molecule X and subsequently undergo either physical or chemical processes:

Physical processes:

Fluorescence:

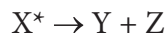


Collisional deactivation:

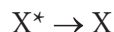


Chemical processes:

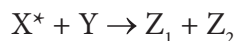
Dissociation:



Isomerization:



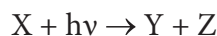
Direct reaction:



Intramolecular rearrangement:



The general form of photolysis reactions:

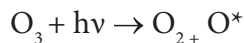


The rate of reaction is:

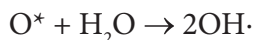
$$-d/dt [X] = d/dt[Y] = d/dt[Z] = k[X]$$

K is the photolysis rate constant for this reaction in units of s^{-1} .

Photolysis occurs in the atmosphere as part of a series of reactions by which primary pollutant nitrogen oxides react to form secondary pollutants such as peroxyacyl nitrate derivatives. The two most important photolysis reactions in the troposphere are:

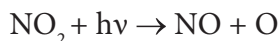


The excited oxygen atom (O^*) can react with water to give the hydroxyl radical:

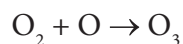
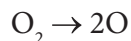


The hydroxyl radical is central to atmospheric chemistry because it can initiate the oxidation of hydrocarbon derivatives in the atmosphere.

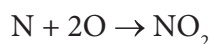
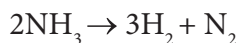
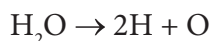
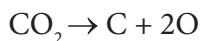
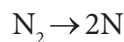
Another reaction involves the photolysis of nitrogen dioxide to produce nitric oxide and an oxygen radical that is a key reaction in the formation of tropospheric ozone:



The formation of the ozone layer is also caused by photolysis. Ozone in the stratosphere is created by ultraviolet light striking oxygen molecules (O_2) and splitting the oxygen molecules into individual oxygen atoms (atomic oxygen). The atomic oxygen then combines with unbroken an oxygen molecule to create ozone (O_3):



In addition, the absorption of radiation in the atmosphere can cause photo-dissociation of nitrogen (as one of several possible reactions) that can lead to the formation of nitric oxide (NO) and nitrogen dioxide (NO₂) that can act as a catalyst to destroy ozone:



As shown in the above equations, most photochemical transformations occur through a series of simple steps (Wayne, 2000; Wayne and Wayne, 2005).

Inorganic Chemical Transformation Reactions – Radioactive Decay

Radionuclides are inorganic chemicals that emit radiation because their atoms are unstable and they disintegrate or decay as they release energy in the form of radioactive particles or waves. There are many different types of radioactive decay. A decay, or loss of energy from the nucleus, results when an atom with an initial type of nucleus (the parent radionuclide or parent radioisotope) transforms into a daughter nuclide. The transformation produces an atom in a different state (a nucleus containing a different number of protons and neutrons). In some decay processes, the parent and the daughter nuclides are different chemical elements, and thus the decay process results in the creation of an atom of a different element (nuclear transmutation). Another type of radioactive decay results in products that are not defined, but appear in a range of molecular fragments of the original nucleus (spontaneous fission) which occurs when a large unstable nucleus spontaneously splits into two (and occasionally three) smaller daughter nuclei, and generally leads to the emission of gamma rays, neutrons, or other particles from those products.

Unlike other inorganic elements or chemicals, radionuclides degrade naturally, but the degradation process itself is hazardous to living things. The risk posed by radionuclides is a function of the type and amount of radiation, as well as exposure pathways. The half-life (the time required to reduce the concentration of a chemical to 50% of the initial concentration) of a radioactive element.

The radioactive half-life for a given radioisotope is a measure of the tendency of the nucleus to decay (disintegrate) and is based upon that probability. The half-life is independent of the physical state (solid, liquid, gas), temperature, pressure, the chemical compound in which the nucleus exists, and essentially any other outside influence. The half-life is also independent of the chemistry of the atomic surface, and independent of the ordinary physical factors of the environment in which the chemical exists.

Inorganic Chemical Transformation Reactions – Rearrangement Reactions

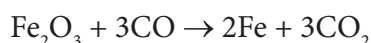
A rearrangement reaction falls into a broad class of (inorganic and organic) reactions where a molecule is rearranged to produce a structural isomer of the original molecule.

Inorganic reactions typically yield products that are in accordance with the generally-accepted mechanism of the reactions. However, in some instances, inorganic reactions do not give exclusively and solely the anticipated products but may lead to other product that arises from an unexpected and mechanistically different reaction path. This type

of unexpected product is often referred to as a rearranged product and, while such a product may not be the expected product, it may be the major product of the reaction. Thus, the reaction has involved a rearrangement of the expected product to an unexpected product – a rearrangement reaction has occurred. More than likely, this may have resulted from a plausible rearrangement occurring during the mechanistic course of the reaction to fulfill the principle of the minimum energy state of the whole system, that is, of the transition state which assumed another configuration to maintain a minimum energy balance to the system. In many cases, the rearrangement affords products of an isomerization, coupled with some stereochemical changes. An energetic requirement is also observed in order for a rearrangement to take place; that is, the rearrangement usually involves an evolution of energy (typically in the form of heat, i.e., the reaction is overall an exothermic reaction) evolution to be able to yield a more stable compound.

Inorganic Chemical Transformation Reactions – Redox Reactions

Redox reactions (reduction-oxidation reactions) are reactions in which one of the reactants is reduced and another reactant is oxidized. Therefore, the oxidation state of the species involved must change. The word reduction originally referred to the loss in weight upon heating a metallic ore such as a metal oxide to extract the metal – the ore was reduced to the metal. However, the meaning of reduction has become generalized to include all processes involving gain of electrons. Thus, in redox reactions, one chemical is oxidized while another chemical is reduced by the net transfer of electron from one chemical to the other. As may be expected, the change in the oxidation states of the oxidized species must be balanced by any changes in the reduced species. For example, the production of iron from the iron oxide ore:



To complicate matters even further, the oxidizing and reducing agents can be the same element or compound, as is the case when disproportionation of the reactive species occurs. For example:



In this equation, n is the number of electrons transferred. Disproportionation reactions do not need to commence with a neutral molecule and can involve more than two species with differing oxidation states.

Within redox reactions, the pair of reactions must always occur, i.e., a reduction reaction must be accompanied by an oxidation process, as electrons are transferred from one chemical to another. Each of the singular reactions in this pair is often referred to as a half-reaction, in which the electrons lost or gained are included explicitly, allowing the electron balance to be counted. The two sides of the reaction, given by the half reactions, should be balanced accordingly. The additional terminology comes from the definition that within redox processes, a reductant transfers electrons to an oxidant, hence, the reductant (reducing agent) loses electrons, so is oxidized, while the oxidant (oxidizing agent) gains electrons, so is reduced.

Inorganic Matter

The inorganic component (mineral matter) of the soil is composed of many types of minerals which influence the properties of the soil. The inorganic material of soil is composed of rock, slowly broken down into smaller particles that vary in size. Soil particles that are 0.1 to 2 mm in diameter are sand. Soil particles between 0.002 and 0.1 mm are called silt, and even smaller particles, less than 0.002 mm in diameter, are called clay. Some soils have no dominant particle size, containing a mixture of sand, silt, and humus; this type of soil is generally referred to as loam.

The weathering of parent rocks and minerals to form the inorganic soil components results ultimately in the formation of inorganic colloids. These colloids are repositories of water and plant nutrients, which may be made available to plants as needed. Inorganic soil colloids often absorb toxic substances in soil, thus playing a role in

detoxification of substances that otherwise would harm plants. The abundance and nature of inorganic colloidal material in soil are obviously important factors in determining soil productivity.

The uptake of plant nutrients by roots involves interactions with the water and inorganic phases. For example, a nutrient held by an inorganic colloid material has to traverse the mineral/water interface and then the water/root interface. This process is often strongly influenced by the ionic structure of soil inorganic matter.

Most common elements in the crust of the Earth are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. Therefore, minerals composed of these elements (particularly silicon and oxygen) constitute most of the mineral fraction of the soil. Common soil mineral constituents are finely divided quartz (SiO_2), orthoclase (KAlSi_3O_8), albite [$\text{NaAlSi}_3\text{O}_8$], epidote [$4\text{CaO}_3(\text{AlFe})_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$], goethite [$\text{FeO}(\text{OH})$], magnetite (Fe_3O_4), calcium carbonate (CaCO_3) and dolomite, the mixed calcium and magnesium carbonates ($\text{CaCO}_3 \cdot \text{MgCO}_3$), and oxides of manganese (MnO) and titanium (TiO).

Instability and Incompatibility

In general, fuel instability and fuel incompatibility can be related to the heteroatom-containing compounds (i.e., nitrogen-, oxygen-, and sulfur-containing compounds) that are present. The degree of unsaturation of the fuel (i.e., the level of olefin species) also plays a role in determining instability/incompatibility. The instability/incompatibility of fuels (from a variety of sources) is manifested in the formation of sludge, sediment, and general darkening in color of the liquid (ASTM D1500).

Sludge (or sediment) formation takes one of the following forms (i) material dissolved in the liquid, (ii) precipitated material, and (iii) material emulsified in the liquid. Under favorable conditions, sludge or sediment will dissolve in the crude oil or product with the potential of increasing the viscosity. Sludge or sediment, which is not soluble in the fuel (ASTM D96, ASTM D473, ASTM D1796, ASTM D2273, ASTM D4007, ASTM D4807, ASTM D4870), may either settle at the bottom of the storage tanks or remain in the crude oil as an emulsion. In most of the cases, the smaller part of the sludge/sediment will settle satisfactorily; the larger part will stay in the liquid as an emulsion. In any case, there is a need of breaking the emulsion, whether it is a water-in-oil emulsion or whether it is the sludge itself, which has to be separated into the oily phase and the aqueous phase. The oily phase can be then processed with the crude oil, and the aqueous phase can be drained out of the system.

Phase separation can be accomplished by either the use of suitable surface active agents allowing for sufficient settling time, or by use of a high voltage electric field for breaking such emulsions after admixing water at a rate of approximately 5% and at a temperature of approximately 100°C (212°F).

Thus, fuels are typically incompatible when sludge, semi-solid, or solid particles (for convenience here, these are termed secondary products to distinguish them from the actual fuel) are formed during and after blending. This phenomenon usually occurs prior to use. If the secondary products are marginally soluble in the blended product, use might detract from solubility of the secondary products and they will appear as sludge or sediment that can be separated by filtration or by extraction (ASTM D4310). When the secondary products are truly insoluble, they separate and settle out as a semi-solid or solid phase floating in the fuel or are deposited on the walls and floors of containers. In addition, secondary products usually increase the viscosity of the crude oil product. Standing at low temperatures will also cause a viscosity change in certain fuels (ASTM D2532).

See also: Incompatibility, Instability and Incompatibility – Methods for Determining.

Instability and Incompatibility – Methods For Determining

Stability/instability and compatibility/incompatibility can be estimated using several tests. These tests are:

1. Compatibility spot tests (ASTM D2781, ASTM D4740).
2. Thermal stability test data (ASTM D873, ASTM D3241).
3. Existent and potential sludge formation (hot filtration test) (ASTM D4870).
4. Asphaltene content (ASTM D3729).

5. The rate of viscosity increase (ASTM D445) of stored residual fuel oil samples at various temperatures with and without exposure to air.
6. Color (ASTM D1500).

In addition to the test for the stability and compatibility of fuels (ASTM D4740), the other most frequently stability test used is the existent and accelerated dry sludge content determination of residual fuels (the hot filtration test). Hot filtration test results of up to 0.2% w/w are considered to be satisfactory; results above 0.4% w/w indicate a poor stability, but differing values might be required, depending on the intended use of the product.

One test, or property, that is somewhat abstract in its application but which is becoming more meaningful popular is the solubility parameter. The solubility parameter allows estimations to be made of the ability of liquids to become miscible on the basis of miscibility of model compound types where the solubility parameter can be measured or calculated.

Although the solubility parameter is often difficult to define when complex mixtures are involved, there has been some progress. For example, crude oil fractions have been assigned a similar solubility parameter to that of the solvent used in the separation. However, there is also the concept that the solubility parameter of crude oil fractions may be defined somewhat differently insofar as they can be estimated from data such as the atomic hydrogen-to-carbon ratios. Whichever method is the best estimate may be immaterial as long as the data are used to the most appropriate benefit and allow some measure of predictability.

Bottle tests constitute the predominant test method, and the test conditions have varied in volume, type of glass or metal, vented and unvented containers, and type of bottle closure. Other procedures have involved stirred reactor vessels under both air pressure or under oxygen pressure, and small volumes of fuel employing a cover slip for solid deposition (ASTM D4625). All of these procedures are gravimetric in nature.

There are several accelerated fuel stability tests that can be represented as a time-temperature matrix. A graphical representation shows that the majority of the stability tests depicted fall close to the solid line, which represents a doubling of test time for each 10°C (18°F) change in temperature. The line extrapolates to approximately one year of storage under ambient conditions. Temperatures at 100°C (212°F) or higher present special chemical problems.

The heteroatom content of the deposits formed in stability studies varied as the source or type of dopant and fuel liquid source varied. This would be an anticipated result. The color changes of both the fuel and the deposits formed are more difficult to interpret.

It is also worthy of note that fractionation of crude oil and its products may also give some indication of instability. There are many schemes by which crude oil and related materials might be fractionated.

There is a series of characterization indices that are present indications of whether or not a crude oil product is stable or unstable. For example, the characterization factor indicates the chemical character of the crude oil and has been used to indicate whether a crude oil was paraffinic in nature or whether it was a naphthenic/aromatic crude oil.

The characterization factor (sometimes referred to as the Watson characterization factor) is a relationship between boiling point and specific gravity:

$$K = T_b^{1/3}/d$$

T_b is the cubic average boiling point, degrees Rankine (°F + 460), and d is the specific gravity at 15.6°C (60°F).

The characterization factor was originally devised to illustrate the characteristics of various feedstocks. Highly paraffinic oils have $K = 12.5$ -13.0, while naphthenic oils have $K = 10.5$ -12.5. In addition, if the characterization factor is above 12, the liquid fuel or product might, because of its paraffinic nature, be expected to form waxy deposits during storage.

See also: Instability and Incompatibility.

Iodine Number

The iodine number (iodine value) is a measure of the iodine absorption by oil under standard conditions and is used to indicate the quantity of unsaturated compounds present. The test method (ASTM D2078) is included in some

specifications and is a measure of fatty acid components or unsaturation either as olefins and/or aromatics. The former are very unlikely to be present in any oil that has undergone sufficient refining to make it colorless, while the aromatic content can be controlled by setting a suitable value for the ultra-violet absorption.

In the test method (ASTM D2078), a sample is dissolved in chloroform and reacted with Wijs solution for 30 minutes in the dark at 25°C. At the end, the solution is mixed with potassium iodide (KI) and titrated with sodium thiosulfate using starch indicator and compared to a blank determination.

Ionic Liquids

An ionic liquid has been defined as a salt that is in the liquid state at ambient temperature, but another definition is that an ionic liquid is a liquid comprised entirely of ions. In fact, any salt that melts without decomposing or vaporizing usually yields an ionic liquid. For example, sodium chloride (NaCl) melts at 801°C (1,474°F) into a liquid that consists largely of sodium cations (Na⁺) and chloride anions (Cl⁻). Conversely, when an ionic liquid is cooled, it often forms an ionic solid which may be either a crystalline solid or a glassy solid. Furthermore, the choice of the cation has a strong impact on the properties of the ionic liquid and will often define the stability. The chemistry and functionality of the ionic liquid is, in general, controlled by the choice of the anion. Free acid of the appropriate anion.

The synthesis of ionic liquids can generally be split into two sections: the formation of the desired cation, and anion exchange where necessary to form the desired product. In some cases, only the first step is required.

Cations synthesis may be carried out either by protonation with a free acid or by quaternarization of an amine or a phosphine, most commonly with an alkyl halogen compound. Alkylation reaction may be carried out with haloalkane derivatives, bromo-alkane derivative derivatives, and iodo-alkane derivative derivatives, with the required reaction conditions becoming less severe in the order Cl < Br < I. The reactivity of the haloalkane also generally decreases with increasing alkyl chain length. The alkylation process possesses the advantages that a wide range of cheap haloalkanes are available, and the substitution reactions generally occur smoothly at even-handed temperatures. Furthermore, the halide salts formed can easily be converted into salts with other anions.

Anion-exchange reactions of ionic liquids can really be divided into two distinct categories which are (i) the direct treatment of halide salts with Lewis acids, and (ii) the formation of ionic liquids by anion metathesis.

The main goal of all anion exchange reactions is the formation of the desired ionic liquid uncontaminated with unwanted cations or anions, a task that is easier for water-immiscible ionic liquids. The synthesis of second-generation ionic liquids, air-stable and water-stable ionic liquids, involved a metathesis reaction between imidazolium halide and a range of silver salts (such as silver nitrate, AgNO₃, silver borofluoride, AgBF₄, silver acetate, AgCH₃CO₂, and silver sulfate, Ag₂SO₄ in methanol or in aqueous methanol solution). The low solubility of silver halide (iodide is the lowest soluble) in these solvents allowed it to be separated simply by filtration, and removal of the reaction solvent allowed isolation of the ionic liquids in high yields and purity. This method has been touted as the most efficient for the synthesis of water-miscible ionic liquids. Complete precipitation of silver halides from organic solvents can also be slow, leading to silver-contaminated products.

Among the various classes of ionic liquids, those containing *N*-heterocyclic cations are most widely used. Imidazolium salts represent the most prominent subclass in this area, and a number of them are commercially available. The solvent properties such as melting points, solubility, and viscosity can easily be tuned in a wide range by varying the substituents at the nitrogen atoms as well as by varying the counter-ions. This makes ionic liquids in general, real designer solvents. Even if imidazolium salts have found very wide application in organic synthesis and catalysis, they have some limitations. One important limitation is that they do not behave as innocent solvents under strongly basic conditions, where they suffer from deprotonation at a carbon atom leading to *N*-heterocyclic carbenes. 1,2,3-Triazolium salts lack an acidic ring-carbon flanked by two nitrogen atoms; consequently, they should be advantageous in this aspect. Unlike 1,2,4-triazolium salts, 1,2,3-triazolium salts were neglected as potential ionic liquids until recently.

In terms of the properties of ionic liquids (Table I-2), they are often moderate-to-poor conductors of electricity, non-ionizing, highly viscous, and frequently exhibit low vapor pressure. The other properties are diverse; for example, many ionic liquids have low combustibility, are thermally stable, with wide liquid regions, and have favorable solvating properties for a range of polar and non-polar compounds.

Table I-2 General properties of ionic liquids.

Property	Comment
A salt	Cation is usually large
A salt	Anion is usually small
Melting point	Preferably below 100°C
Freezing point	Preferably below 100°C
Liquid range	>200°C
Thermal stability	High
Viscosity	<100 cP
Dielectric constant	<30
Polarity	Moderate
Solvent properties	Good
Catalytic properties	Good
Vapor pressure	Low-to-negligible

In the energy field, ionic liquids have many potential applications, such as they are powerful solvents and can be used as electrolytes (Table I-3). In fact, salts that are liquid at near-ambient temperature are important for electric battery applications.

Table I-3 Examples of the uses of ionic liquids in the alternative energy field.

Electrolytes
Batteries
Fuel cells
Separation
Extraction
Extractive distillation
Gas separation
Membranes
Lubricants and additives
Fuel additives
Lubricants
Heat storage
Thermal fluids
Solvents
Bio-catalysts
Catalysts
Polymerization

Also, the ionic liquid 1-butyl-3-methylimidazolium chloride has been investigated for the recovery of uranium and other metals from spent nuclear fuel and other sources. Protonated betaine bis(trifluoro-methane sulfonyl) imide has been investigated as a solvent for uranium oxides. The ionic liquids, n-butyl-n-methyl pyrrolidinium bis(trifluoro methyl sulfonyl)imide and n-methyl-n-propyl piperidinium bis(trifluoromethyl sulfonyl)imide, have been investigated for the electrodeposition of europium and uranium metals, respectively.

Ionic liquids are also potential heat transfer and storage media in solar thermal energy systems. Concentrating solar thermal facilities such as parabolic troughs and solar power towers focus the sun's energy onto a receiver which can generate temperatures on the order of around 600°C (1,110°F). This heat can then generate electricity in a steam or other cycle. For buffering during cloudy periods or to enable generation overnight, energy can be stored by heating an intermediate fluid. Although nitrate salts have been the medium of choice since the early 1980s, they freeze at a temperature on the order of 220°C (430°F) and thus require heating to prevent solidification.

Ionic liquids can aid the recycling of synthetic goods, plastics, and metals and offer the specificity required to separate similar compounds from each other, such as separating polymeric substances from plastic waste streams which can help avoid incinerating plastics or discharging them in a landfill.

However, while the low volatility of ionic liquids eliminates a major pathway for environmental release and contamination, the aquatic toxicity of ionic liquids is at least as severe (or even more so) than many solvents. Moreover, balancing the reduction of volatile organic compounds (VOCs) against waterway spills (via waste ponds/streams) requires caution because the diversity of ionic liquids simplifies the process of identifying compounds that meet safety requirements.

Iogen Process

The production of alcohol for fuels (as well as for petrochemical uses) from cellulosic biomass is of growing interest around the world. Cellulosic biomass can be used to produce transportation fuel, with the overall process having little net production of greenhouse gases. Biomass is available as a by-product of many industrial processes and agricultural materials, or can be potentially produced from dedicated energy crops.

The Iogen process is an enzymatic hydrolysis process for converting lignocellulose materials to ethanol. The unique aspects of the technology include the steam explosion pre-treatment that was pioneered by Iogen, and the proprietary enzymes developed, manufactured, and marketed by Iogen. The cellulose hydrolysis is an expensive but effective option and not economically feasible for all ethanol producers.

The process is currently suitable for agricultural residues such as wheat straw and corn straw. Hardwood residues are also a suitable feedstock. A single step pre-treatment process for agricultural and hardwood residues can produce a material that can be efficiently hydrolyzed by the enzymes. The pre-treatment process is not as effective for separating the lignin of softwoods from the cellulosic material.

The process will produce lignin as a co-product. The relatively mild pre-treatment process employed should provide a lignin that can be utilized as a starting material in other processes.

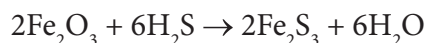
Iron Oxide Process

The iron oxide process (iron sponge process, dry box process) is the oldest and most widely used batch process for sweetening of natural gas and natural gas liquids. The process was implemented during the 19th century and has been in use in Europe and the United States for over 100 years. Hydrogen sulfide scavengers are appropriate for use at the low concentrations of hydrogen sulfide where conventional chemical absorption and physical solvents are not economical.

In the process, gas is passed through a bed of wood chips impregnated with iron oxide to scavenge hydrogen sulfide and organic sulfur compounds (mercaptans) from natural gas streams. The iron sponge method is a semi-continuous system employing two steel drums as main equipment, packed with wood shavings impregnated with iron oxide.

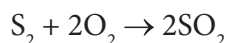
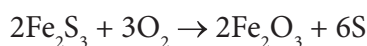
The iron sponge process is considered a selective process removing only hydrogen sulfide and small traces of carbonyl sulfide and carbon disulfide. The basis of the operation is the chemical reaction of the H_2S content in the stream with the hydrated iron oxide to form iron sulfide.

The *sponge* consists of wood shavings impregnated with a hydrated form of iron oxide. The wood shavings serve as a carrier for the active iron oxide powder. Hydrogen sulfide is removed by reacting with iron oxide to form ferric sulfide. The process is usually best applied to gases containing low-to-medium concentrations (300 ppm) of hydrogen sulfide or mercaptans. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is high purity. The use of iron sponge process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:



The reaction requires the presence of slightly alkaline water and a temperature below 43°C (110°F), and bed alkalinity should be checked regularly, usually on a daily basis. A pH level on the order of 8-10 should be maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the inlet gas stream.

The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:



The regeneration step, i.e., the reaction with oxygen is exothermic and air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly, the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles, this sulfur will form a cake over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles, the bed must be removed and a new bed introduced into the vessel.

In some designs, the iron sponge may be operated with continuous regeneration by injecting a small amount of air into the sour gas feed. The air regenerates ferric sulfide, while hydrogen sulfide is removed by ferric oxide. This process is not as effective at regenerating the bed as the batch process and requires a higher-pressure air stream.

In the process, the sour gas should pass down through the bed. In the case where continuous regeneration is to be utilized, a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the on-stream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove. The number of vessels containing iron oxide can vary from one to four. In a two-vessel process, one of the vessels would be on stream removing hydrogen sulfide from the sour gas while the second vessel would either be in the regeneration cycle or having the iron sponge bed replaced.

When periodic regeneration is used, a tower is operated until the bed is saturated with sulfur and hydrogen sulfide begins to appear in the sweetened gas stream. At this point, the vessel is removed from service and air is circulated through the bed to regenerate the iron oxide. Regardless of the type of regeneration process used, a given iron oxide bed will lose activity gradually and eventually will be replaced. For this reason, the reactor vessels should be designed to minimize difficulties in replacing the iron sponge in the beds. The change out of the beds is hazardous. Exposure to air when dumping a bed can cause a sharp rise in temperature, which can result in spontaneous combustion of the bed. Care must be exercised in opening the tower to the air. The entire bed should be wetted before beginning the change out operation.

Iron oxide reactors have taken on a number of configurations from conventional box vessels to static tower purifiers. The selection depends upon the process application. Static tower purifiers are used in high-pressure applications,

since a longer bed depth gives a greater efficiency, and the total pressure drop is a smaller fraction of the available pressure. Static tower purifiers are also fitted with trays to eliminate compaction for lower-pressure applications. Conventional boxes consist of large rectangular vessels, either built into the ground, or supported on legs to save footprint. They are composed of several layers, with a typical bed depth of at least two feet.

Iron oxide suspensions, like iron oxide slurries, rely upon hydrated ferric oxide as the active regenerable agent. However, iron oxide suspensions react in a basic environment with an alkaline compound, followed by the reaction of the hydrosulfide with iron oxide to form iron sulfide. The iron is then regenerated by aeration.

Generally, the iron oxide process is suitable only for small-to-moderate quantities of hydrogen sulfide. Approximately 90% of the hydrogen sulfide can be removed per bed, but bed clogging by elemental sulfur occurs, and the bed must be discarded, and the use of several beds in series is not usually economical. Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stretford process. The *Ferrox process* is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid.

The gas stream should be wet when passing through an iron sponge bed as drying of the bed will cause the iron sponge to lose its capacity for reactivity. If the gas is not already water-saturated or if the influent stream has a temperature greater than 50°C (approximately 120°F), water with soda ash is sprayed into the top of the contactor to maintain the desired moisture and alkaline conditions during operation.

During recent years, hydrogen sulfide scavenger technology has been expanded with many new materials coming on the market and others being discontinued. Overall, the simplicity of the process, low capital costs, and relatively low chemical (iron oxide) cost continue to make the process an ideal solution for hydrogen sulfide removal.

See also: Gas Cleaning, Iron Oxide Slurry Process, Iron Oxide Suspension, Iron Sponge Process.

Iron Oxide Slurry Process

The process is designed to remove hydrogen sulfide from natural gas streams and uses iron oxide powder suspended in an aqueous column. Hydrogen sulfide in the gas stream reacts with the iron oxide as the gas stream is bubbled up through the suspension. The reactions of the iron oxide slurry are similar to those for dry iron oxide processes, except with a higher proportion of the magnetite form of iron oxide (Fe_3O_4) (Slurrisweet process).

An iron oxide slurry was used in conjunction with a silicon-based defoamer with additives and a dispersant to reduce potential problems due to foaming, rapid settling of suspended iron oxide particles, and short batch life. Corrosion was inhibited by using an epoxy coating on the vessel. Injection of air at 5% mole concentration of hydrogen sulfide extended the batch life and stabilized the spent chemical.

Advantages of the process include its ability to selectively remove hydrogen sulfide from a natural gas stream containing carbon dioxide. Furthermore, the process offers a scheme of sweetening without the undesirable side effects of emission of sulfur dioxide and spent batch disposal problems.

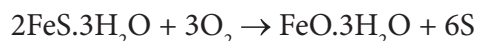
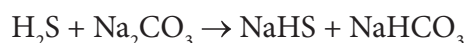
However, there are disadvantages of the slurry process that relate to: (i) carry-over of oxide slurry from the contactor tower, (ii) occasional failure of a fresh slurry batch to sweeten below the hydrogen sulfide sale gas sales specification, (iii) inconsistent and short batch life, (iv) rapid settling of oxide powder at low production rates, (v) inability to remove all of spent slurry solids from contactor, leaving plugged tower packing and promoting subsequent channeling of gas, and (vi) fouling of valve seats and plugging small lines.

These disadvantages can be eliminated by employing both mechanical and chemical alterations. Additives have been shown to be effective in eliminating carry-over improving the suspension properties of the slurry oxide. This also allows for better removal of expended slurry solids during batch change outs. Controlled injection of trace amounts of air into the sour gas stream has resulted in substantially longer slurry batch life and considerably lower hydrogen sulfide in the product gas.

See also: Iron Oxide Process, Iron Oxide Slurry Process, Iron Sponge Process, Zinc Oxide Process.

Iron Oxide Suspension Process

Iron oxide suspensions, like iron oxide slurries, rely upon hydrated ferric oxide as the active regenerable agent. However, iron oxide suspensions react in a basic environment with an alkaline compound, followed by the reaction of the hydrosulfide with iron oxide to form iron sulfide; the iron is then regenerated by aeration.

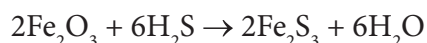


Iron oxide suspensions are the precursors to the chelated iron used in iron chelate solutions for chelate processes.

Iron Sponge Process

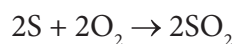
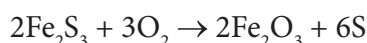
Hydrogen sulfide scavengers have been used for many years. An example is the iron sponge process (*iron oxide process, dry box process*) that is the oldest and still the most widely used batch process for sweetening of natural gas and natural gas liquids. The process was implemented during the 19th century and has been in use in Europe and the United States for over 100 years. Hydrogen sulfide scavengers are appropriate for use at the low concentrations of hydrogen sulfide where conventional chemical absorption and physical solvents are not economical. During recent years, hydrogen sulfide scavenger technology has been expanded with many new materials coming on the market and others being discontinued. Overall, the simplicity of the process, low capital costs, and relatively low chemical (iron oxide) cost continue to make the process an ideal solution for hydrogen sulfide removal.

The *sponge* consists of wood shavings impregnated with a hydrated form of iron oxide. The wood shavings serve as a carrier for the active iron oxide powder. Hydrogen sulfide is removed by reacting with iron oxide to form ferric sulfide. The process is usually best applied to gases containing low-to-medium concentrations (300 ppm) of hydrogen sulfide or mercaptans. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is high purity. The use of iron sponge process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:



The reaction requires the presence of slightly alkaline water and a temperature below 43°C (110°F), and bed alkalinity should be checked regularly, usually on a daily basis. A pH level on the order of 8-10 should be maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the inlet gas stream.

The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:



The regeneration step, i.e., the reaction with oxygen is exothermic, and air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly, the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles, this sulfur will form a cake

over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles, the bed must be removed and a new bed introduced into the vessel.

In the process, the sour gas should pass down through the bed. In the case where continuous regeneration is to be utilized, a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the on-stream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove. In some designs, the iron sponge may be operated with continuous regeneration by injecting a small amount of air into the sour gas feed. The air regenerates ferric sulfide while hydrogen sulfide is removed by ferric oxide. This process is not as effective at regenerating the bed as the batch process and requires a higher-pressure air stream. Also, the number of vessels containing iron oxide can vary from one to four. In a two-vessel process, one of the vessels would be on stream removing hydrogen sulfide from the sour gas, while the second vessel would either be in the regeneration cycle or having the iron sponge bed replaced.

When periodic regeneration is used, a tower is operated until the bed is saturated with sulfur and hydrogen sulfide begins to appear in the sweetened gas stream. At this point, the vessel is removed from service and air is circulated through the bed to regenerate the iron oxide. Regardless of the type of regeneration process used, a given iron oxide bed will lose activity gradually and eventually will be replaced. For this reason, the reactor vessels should be designed to minimize difficulties in replacing the iron sponge in the beds. The change out of the beds is hazardous. Exposure to air when dumping a bed can cause a sharp rise in temperature, which can result in spontaneous combustion of the bed. Care must be exercised in opening the tower to the air. The entire bed should be wetted before beginning the change out operation.

Iron oxide reactors have taken on a number of configurations from conventional box vessels to static tower purifiers. The selection depends upon the process application. Static tower purifiers are used in high-pressure applications, since a longer bed depth gives a greater efficiency, and the total pressure drop is a smaller fraction of the available pressure. Static tower purifiers are also fitted with trays to eliminate compaction for lower-pressure applications. Conventional reactors consist of large rectangular vessels, either built into the ground, or supported on legs to save footprint. They are composed of several layers, with a typical bed depth of at least two feet.

Iron oxide suspensions, like iron oxide slurries, rely upon hydrated ferric oxide as the active regenerable agent. However, iron oxide suspensions react in a basic environment with an alkaline compound, followed by the reaction of the hydrosulfide with iron oxide to form iron sulfide. The iron is then regenerated by aeration.

Generally, the iron oxide process is suitable only for small-to-moderate quantities of hydrogen sulfide. Approximately 90% of the hydrogen sulfide can be removed per bed, but bed clogging by elemental sulfur occurs and the bed must be discarded and the use of several beds in series is not usually economical. Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stretford process. The *Ferrox process* is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid.

The natural gas should be wet when passing through an iron sponge bed as drying of the bed will cause the iron sponge to lose its capacity for reactivity. If the gas is not already water-saturated or if the influent stream has a temperature greater than 50°C (approximately 120°F), water with soda ash is sprayed into the top of the contactor to maintain the desired moisture and alkaline conditions during operation.

See also: Gas cleaning, Iron Oxide Process, Iron Oxide Slurry Process, Iron Oxide Suspension.

Isotopes

The term isotope is a form of a chemical element that is characterized by the same number of protons but different numbers of neutrons in their nucleus. An isotope shares the same atomic number and location in the periodic table, but have distinct atomic weights.

Thus, an isotope is an atom of an element that have the usual number of protons but different numbers of neutrons in their nuclei. For example, twelve protons and twelve neutrons make up the nucleus of the element carbon. One isotope of carbon, C-14, has twelve protons and fourteen neutrons in its nucleus.

Using hydrogen as the example, there are three isotopes of the element which are (i) hydrogen, (ii), deuterium, and (iii) tritium. How do we distinguish between them which each have one single proton but differ in the number of the neutrons? Hydrogen has no neutron, deuterium has one neutron, and tritium has two neutrons. Some elements, such as carbon, potassium, and uranium, have naturally occurring isotopes. Carbon-12 (^{12}C), the most common isotope of carbon, contains six protons and six neutrons.

Radioisotopes such as carbon-14 (C-14, ^{14}C) are unstable isotopes, and the nuclei of such isotopes decay (break apart) at a steady rate. Decaying radioisotopes produce other isotopes as they emit energy and/or high-energy particles. If the newly formed nuclei are radioactive as well, they emit radiation and change into other nuclei. The final products in this chain are stable, nonradioactive nuclei.

See also: Hydrogen, Deuterium, Radioactivity. Tritium.

ITSL Process

The integrated two-stage liquefaction process (ITSL process) has received considerable attention as one of the most promising technology indirect coal liquefaction.

The process consists of a slurry preparation step and followed by hydrotreated solvent recovery and a solvent deashing system. The system was integrated by the recycle of the resid, hydrotreated solvent, and low-pressure flash bottoms containing ash, unconverted coal, hydrotreated resid, and hydrotreated solvent. Solids recycle allows an increased concentration of solids in the feedstock and hence a lower feed rate. The solvent recovery system consists of atmospheric flash and vacuum flash equipment.

The process lends itself to the conversion of biomass (either alone or with a carbonaceous feedstock such as coal) to fuel products, and the biomass can also be used as a hydrogen source via gasification to compensate for the any deficit in process hydrogen.

See also: Gasification, Gasification of Biomass.

Jatropha

Jatropha is a small but versatile bush/tree from the Euphorbiaceae family. The tree flowers and produces clusters of approximately 10 to 15 fruits with a seed containing high concentrations of oil. *Jatropha curcas* L. is gaining a lot of attention as a potential feedstock for biodiesel production due to its high oil content and ability to grow in less than ideal conditions. However, harvesting and logistical challenges have kept the plant from being grown in large-scale production in places where there is not an abundance of low-cost labor. Historically, most of the Jatropha has been grown in tropical areas including Africa and Asia, especially India. More recently, it has been grown on most continents around the world. The green shading on the map below indicates the primary areas where Jatropha is grown. These areas are mainly inside the tropics and are not known to have land of good quality.

This low maintenance plant has generally proven to be resistant to local pests under common cultivation practices and can produce seeds containing up to 40% oil. While Jatropha is touted as being able to survive in poor soils with only small amounts of fertilizer and water; the fruit (and thus oil) yields increase significantly with increased soil fertility and water. For example, adding small amounts of magnesium, sulfur, and calcium have a significant impact on improving yields. Jatropha can survive in areas with annual rainfall of 8 to 12 inches. In extreme conditions, plants will survive drought by dropping its leaves to reduce transpiration loss. In fact, this resilient plant can survive three full years of drought before it would die. However, fruit production is low to minimal during these drought years. While Jatropha is most commonly grown in low altitude regions that are relatively warm, it can grow at higher altitudes but can only handle a slight frost.

See also: Jatropha Oil.

Jatropha Oil

The use of biodiesel as an alternative fuel is becoming increasingly popular, and the interest in using Jatropha as a non-edible oil feedstock is rapidly growing. Jatropha oil is vegetable oil produced from the seeds of the *Jatropha curcas*, a plant that can grow in marginal lands and common lands. When Jatropha seeds are crushed, the resulting Jatropha oil can be processed to produce a high-quality biodiesel that can be used in a standard diesel car, while the residue (press cake) can also be processed and used as biomass feedstock to power electricity plants or used as fertilizer (it contains nitrogen, phosphorus, and potassium). The plant may yield more than four times as much fuel per acre as soybean, and more than ten times that of maize (corn).

Jatropha curcas is considered to be as one of the best candidates for future biodiesel production. The performance of the engine using blends of diesel and Jatropha oil and significant improvement in performance of a single cylinder was observed compared to vegetable oil alone. The specific fuel consumption and the exhaust gas temperature were reduced due to decrease in viscosity of the vegetable oil. Acceptable thermal efficiencies of the engine were obtained with blends containing up to 50% volume of Jatropha oil. From the properties and engine test results, a 40 to 50% v/v blend of Jatropha oil can be substituted for diesel without any engine modification.

Different methods can be used to obtain Jatropha oil from the seeds – the common methods used for the extraction of the oil include (i) mechanical pressing, (ii) supercritical fluid extraction, and (iv) solvent extraction. Biodiesel is produced from Jatropha oil by transesterification which involves altering the chemical properties of a vegetable oil by using methanol. Transesterification of vegetable oil is a relatively simple process that yields high conversion with glycerin as the only by-product.

See also: Biodiesel, Jatrophas, Transesterification, Vegetable Oil.

Jerusalem Artichoke

The Jerusalem artichoke (*Helianthus tuberosus*, also called sunroot, sunchoke, or earth apple) is a species of sunflower that is native to central North America. It is a herbaceous perennial plant that grows up to 5 to 10 feet tall with opposite leaves on the upper part of the stem but alternate below. The leaves have a rough, hairy texture. Larger leaves on the lower stem are broad-ovoid-acute and can be up to 12 inches long, while the leaves higher on the stem are smaller and narrower. The tubers are often elongated and uneven, typically 3 to 4 inches long and 1 to 2 inches thick with a crisp and crunchy texture when raw. They vary in color from pale brown to white, red, or purple.

The Jerusalem artichoke has shown excellent potential as an alternative sugar crop. A member of the sunflower family, this crop is native to North America and well-adapted to northern climates. Like the sugar beet, the Jerusalem artichoke produces sugar in the top growth and stores it in the roots and tuber. It can grow in a variety of soils, and it is not demanding of soil fertility. The Jerusalem artichoke is a perennial; small tubers left in the field will produce the next seasonal crop, so no ploughing or seeding is necessary. The high-fructose syrups that can be derived from the tubers produced by the *Jerusalem artichoke* may be used for the production of ethanol and other industrial raw materials. Jerusalem artichokes also produce a large amount of top growth which may also prove to be a useful source of biomass for energy purposes.

The crop is relatively easy to grow but difficult to harvest and store. The tubers are tightly attached to the crown of the plant and, when dug by machine, come up as a mass of tubers, crown tissue, and soil which does not separate well like potato or sweet potato. Thus, much hand labor was needed for harvest. In addition to that, the tubers do not store well after digging and must be utilized quickly to prevent spoilage and loss. However, the tubers do keep well in the soil and presumably could be stored in the field and dug as needed whenever the soil was not too wet.

See also: Energy Crops.

Kerosene

Kerosene (kerosine; lamp oil), also called paraffin or paraffin oil, is a flammable pale-yellow or colorless oily liquid with a characteristic odor. It is obtained from petroleum and used for burning in lamps and domestic heaters or furnaces, as a fuel or fuel component for diesel fuel and jet fuel, and as a solvent for greases and insecticides.

Kerosene is intermediate in volatility between gasoline and gas/diesel oil. It is a medium-boiling oil distilling between 150 and 300°C (300 to 570°F). Kerosene has a flash point about 25°C (77°F) and is suitable for use as an illuminant when burned in a wide lamp. The term *kerosene* is also too often incorrectly applied to various fuel oils, but a fuel oil is actually any liquid or liquid petroleum product that produces heat when burned in a suitable container or that produces power when burned in an engine.

Kerosene was the major refinery product before the onset of the *automobile age*, but now kerosene can be termed one of several secondary petroleum products after the primary refinery product – gasoline. Kerosene originated as a straight-run petroleum fraction that boiled between approximately 205 and 260°C (400 to 500°F). Some crude oils, for example those from the Pennsylvania oil fields, contain kerosene fractions of high quality, but other crude oils, such as those having an asphalt base, must be thoroughly refined to remove aromatics and sulfur compounds before a satisfactory kerosene fraction can be obtained.

Composition

Chemically, kerosene is a mixture of hydrocarbons; the chemical composition depends on its source, but it usually consists of about 10 different hydrocarbons, each containing from 10 to 16 carbon atoms per molecule; the constituents include *n*-dodecane ($n\text{-C}_{12}\text{H}_{26}$), alkyl benzenes, and naphthalene and its derivatives. Kerosene is less volatile than gasoline; it boils between about 140°C (285°F) and 320°C (610°F).

Kerosene is intermediate in volatility between gasoline and gas/diesel oil. It is a medium oil distilling between 150 and 300°C (300 to 570°F). Kerosene has a flash point about 25°C (77°F) and is suitable for use as an illuminant when burned in a wide lamp. The term *kerosene* is also too often incorrectly applied to various fuel oils, but a fuel oil is actually any liquid or liquid petroleum product that produces heat when burned in a suitable container or that produces power when burned in an engine.

Kerosene, because of its use as a burning oil, must be free of aromatic and unsaturated hydrocarbons, as well as free of the more obnoxious sulfur compounds. The desirable constituents of kerosene are saturated hydrocarbons, and it is for this reason that kerosene is manufactured as a straight-run fraction, not by a cracking process.

Manufacture

Kerosene was first manufactured in the 1850s from coal tar, and the name coal oil is often applied to kerosene, but petroleum became the major source after 1859. From that time, the kerosene fraction is, and has remained, a distillation fraction of petroleum. However, the quantity and quality vary with the type of crude oil, and although some crude oils yield excellent kerosene quite simply, others produce kerosene that requires substantial refining.

Kerosene is now largely produced by cracking the less volatile portion of crude oil at atmospheric pressure and elevated temperatures. In the early days of kerosene production, the poorer-quality kerosene was treated with large quantities of sulfuric acid to convert them to marketable products. However, this treatment resulted in high acid and kerosene losses, but the later development of the *Edeleanu* process overcame these problems.

Kerosene is a very stable product, and additives are not required to improve the quality. Apart from the removal of excessive quantities of aromatics by the *Edeleanu* process, kerosene fractions may need only a lye wash or a doctor treatment if hydrogen sulfide is present to remove mercaptans.

Properties and Use

Kerosene is by nature a fraction distilled from petroleum that has been used as a fuel oil from the beginning of the petroleum-refining industry. As such, low proportions of aromatic and unsaturated hydrocarbons are desirable to maintain the lowest possible level of smoke during burning. Although some aromatics may occur within the boiling range assigned to kerosene, excessive amounts can be removed by extraction; that kerosene is not usually prepared from cracked products almost certainly excludes the presence of unsaturated hydrocarbons.

The essential properties of kerosene are flash point, fire point, distillation range, burning, sulfur content, color, and cloud point. In the case of the flash point (ASTM D56), the minimum flash temperature is generally placed above the prevailing ambient temperature; the fire point (ASTM D92) determines the fire hazard associated with its handling and use.

The boiling range (ASTM D86) is of less importance for kerosene than for gasoline, but it can be taken as an indication of the viscosity of the product, for which there is no requirement for kerosene. The ability of kerosene to burn steadily and cleanly over an extended period (ASTM D187) is an important property and gives some indication of the purity or composition of the product.

The significance of the total sulfur content of a fuel oil varies greatly with the type of oil and the use to which it is put. Sulfur content is of great importance when the oil to be burned produces sulfur oxides that contaminate the surroundings. The color of kerosene is of little significance, but a product darker than usual may have resulted from contamination or aging, and in fact a color darker than specified (ASTM D156) may be considered by some users as unsatisfactory. Finally, the cloud point of kerosene (ASTM D2500) gives an indication of the temperature at which the wick may become coated with wax particles, thus lowering the burning qualities of the oil.

See also: Refining.

Kinematic Viscosity

The kinematic viscosity of a liquid is the ratio of viscosity to density, both measured at the same temperature and can be obtained by dividing the absolute viscosity of a fluid with the mass density of the fluid:

$$\nu = \mu/\rho$$

ν is the kinematic viscosity, μ is the absolute or dynamic viscosity, and ρ is the density.

In the SI-system, the theoretical unit is m^2/s or commonly used Stoke (St)

$$1 \text{ St} = 10^{-4} \text{ m}^2/\text{s}$$

The Stoke is an impractical large unit; it is usually divided by 100 to give the unit called Centistokes (cSt):

$$1 \text{ St} = 100 \text{ cSt}$$

$$1 \text{ cSt} = 10^{-6} \text{ m}^2/\text{s}$$

Since the specific gravity of water at 20.2°C (68.4°F) is almost unity, the kinematic viscosity of water at 20.2°C (68.4°F) is 1.0 cSt.

The viscosity of a fluid is highly temperature dependent, and for either dynamic or kinematic viscosity to be meaningful, the reference temperature must be quoted. The usual reference temperature for a residual fluid is 100°C (212°F), and for a distillate fluid, the usual reference temperature is 40°C (104°F). For a liquid, the kinematic viscosity will decrease with an increase in temperature, but for a gas, the kinematic viscosity will increase with increase in temperature.

Saybolt Universal Seconds (SUS) is used to measure viscosity. The efflux time is Saybolt Universal Seconds (SUS) required for 60 milliliters of a petroleum product to flow through the calibrated orifice of a Saybolt Universal

viscometer, under carefully controlled temperature (ASTM D88). This method has largely been replaced by the kinematic viscosity method.

Kinematic viscosity versus dynamic or absolute viscosity can be expressed as:

$$\nu = 4.63\mu/(\text{specific gravity})$$

ν is the kinematic viscosity (SSU), μ is the dynamic or absolute viscosity (cP), and SG is the specific gravity.

Koppers-Totzek Gasifier

The Koppers-Totzek gasifier is a commercially established, high-temperature, entrained flow gasifier capable of partially oxidizing a wide variety of feed stocks at pressures slightly above atmospheric.

Biomass gasification is an old technology that is viewed as an alternative to conventional fuel. In the gasification process, wood, charcoal, and other biomass materials are gasified to produce the so-called 'producer gas' for power or electricity generation. Gasification system basically consists of a gasifier unit, purification system, and energy converters – burner or engine.

A wide range of biomass fuels such as wood, charcoal, wood waste (branches, roots, bark, saw dust) as well as agricultural residues – maize cobs, coconut shells, cereal straws, and rice husks – can be used as fuel for biomass gasification. Theoretically, almost all kinds of biomass with moisture content of 5 to 30% can be gasified; however, not every biomass fuel leads to successful gasification.

The gasifier has two-headed burner, has heads 180° apart, and is about 24 feet high and has an inside diameter of up to 3.5 m. A four-headed gasifier, with burners 90° apart. The burner heads are opposed to ensure that particles escaping from one burner will be burnt in the opposite burner. Carbon is oxidized in the gasifier producing a high-temperature flame zone of about 1,900°C (3,450°F). Heat losses and the endothermic carbon-steam reactions reduce the exit temperature to around 1,500°C (2,730°F). The feedstock is gasified nearly to completion in times or the order of 1 second. Carbon conversion, dependent on the reactivity of the feedstock, is about 96 to 98%. At the prevailing high operating temperatures, gaseous and vaporous hydrocarbons emanating from the feedstock decompose so rapidly that coagulation of feedstock particles during the plastic stage does not occur. Thus, any feedstock can be gasified regardless of its caking property, ash content, or ash fusion temperature.

Also, only gaseous products are produced; no tars, condensable hydrocarbons, or phenols are formed. Approximately 50% of the mineral matter drops out as slag. The remainder of the ash leaves the gasifier as fine slag particles entrained in the exit gas. Gas leaving the gasifier may be directly water quenched to solidify entrained slag droplets, if necessary, before passing through a waste heat boiler where high pressure steam is produced. The gas exits the waste heat boiler at 175 to 260°C (340 to 500°F).

The gasifier is, in many ways, similar to the Texaco gasifier. The feedstock is dried, pulverized, and conveyed with nitrogen from storage to the gasifier service bin and feed bins. Variable-speed feedstock screw feeders then continuously discharge the feedstock into a mixing nozzle, where a mixture of steam and oxygen entrains the pulverized feedstock. Moderate temperature and high burner velocity prevent oxidation of the feedstock.

See also: Gasification, Gasification of Biomass.

Koppers-Totzek Gasifier – Biomass Gasification

Biomass gasification is an old technology that is viewed as an alternative to conventional fuel. In the gasification process, wood, charcoal, and other biomass materials are gasified to produce the so-called 'producer gas' for power or electricity generation. Gasification system basically consists of a gasifier unit, purification system, and energy converters – burner or engine.

A wide range of biomass fuels such as wood, charcoal, wood waste (branches, roots, bark, saw dust) as well as agricultural residues – maize cobs, coconut shells, cereal straws, and rice husks – can be used as fuel for biomass

gasification. Theoretically, almost all kinds of biomass with a moisture content of 5 to 30% can be gasified; however, not every biomass fuel leads to successful gasification.

The gasifier is a refractory-lined steel shell (equipped with a steam jacket for producing low-pressure process steam) that is commonly used to process coal. A two-headed burner has heads 180° apart, and the gasifier is about 24 feet high and has an inside diameter of up to 3.5 m. The burner heads are opposed to ensure that particles escaping from one burner will be burnt in the opposite burner. Carbon is oxidized in the gasifier producing a high temperature flame zone of approximately 1,900°C (3,450°F). Heat losses and the endothermic carbon-steam reactions reduce the exit temperature to around 1,500°C (2,730°F).

The feedstock is gasified nearly to completion in times or the order of 1 second. Carbon conversion, dependent on the reactivity of the feedstock, is about 96 to 98%. At the prevailing high operating temperatures, gaseous and vaporous hydrocarbons emanating from the feedstock decompose so rapidly that coagulation of feedstock particles during the plastic stage does not occur. Thus any feedstock can be gasified regardless of its caking property, ash content, or ash fusion temperature.

Also, only gaseous products are produced; no tars, condensable hydrocarbons, or phenols are formed. Approximately 50% of the feedstock ash drops out as slag. The remainder of the ash leaves the gasifier as fine slag particles entrained in the exit gas. Gas leaving the gasifier may be directly water-quenched to solidify entrained slag droplets, if necessary, before passing through a waste heat boiler where high pressure steam is produced. The gas exits the waste heat boiler at 175 to 260°C (345 to 500°F).

The gasifier is, in many ways, similar to the Texaco gasifier. The feedstock is dried, pulverized, and conveyed with nitrogen from storage to the gasifier service bin and feed bins. Variable-speed feedstock screw feeders then continuously discharge the feedstock into a mixing nozzle, where a mixture of steam and oxygen entrains the pulverized feedstock. Moderate temperature and high burner velocity prevent oxidation of the feedstock.

See also: Gasification, Gasification of Biomass.

Koppers-Totzek Process

The Koppers-Totzek process is, perhaps the best known of the entrained-solids processes and operates at atmospheric pressure. The reactor is a relatively small, cylindrical, refractory-lined vessel into which feedstock, oxygen, and steam are charged. The reactor typically operates at an exit temperature of about 1,480°C (2,700°F), and the pressure is maintained slightly above atmospheric pressure.

Gases and vaporized hydrocarbons produced by the feedstock at medium temperatures immediately pass through a zone of high temperature in which they decompose so rapidly that feedstock particles in the plastic stage do not agglomerate, and thus any type of feedstock can be gasified irrespective of caking tendencies, ash content, or ash fusion temperature. The gas product contains no ammonia, tars, phenols, or condensable and can be upgraded to synthesis gas by reacting all or part of the carbon monoxide content with steam to produce additional hydrogen plus carbon dioxide.

The Koppers-Totzek process is an entrained-solids process which operates at atmospheric pressure. The reactor is a cylindrical, refractory-lined feedstock burner into which feedstock, oxygen, and steam are charged through at least two burner heads.

The feed feedstock for the process is crushed (so that 70% will pass through a 200-mesh screen), mixed with oxygen and low-pressure steam, and injected into the gasifier through a burner head. The heads are spaced 180 or 90° apart (representing two-headed or four-headed opposed burner arrangements) and are designed such that steam envelopes the flame and protects the reactor walls from excessive heat.

The reactor typically operates at an exit temperature of approximately 1,480°C (2,700°F), and the pressure is maintained just slightly above atmospheric. Only about 85 to 90% of the total carbon may be gasified in a single pass through the gasifier because carbon conversion is a function of the reactivity of the feedstock and approaches 100% for lignite.

The heat in the reactor causes the formation of slag from mineral ash, and this is removed from the bottom of the gasifier through a water seal. Gases and vaporized hydrocarbons produced by the feedstock at medium temperatures immediately pass through a zone of high temperature in which they decompose so rapidly that feedstock particles in

the plastic stage do not agglomerate, and thus any type of feedstock can be gasified irrespective of caking tendencies, ash content, or ash fusion temperature.

In addition, the high operating temperature ensures that the gas product contains no ammonia, tars, phenols, or condensable hydrocarbons. The raw gas can be upgraded to synthesis gas by reacting all or part of the carbon monoxide content with steam to produce additional hydrogen plus carbon dioxide.

See also: Gasification, Gasification of Biomass.

Kopp's Law

Kopp's law refers to either of two relationships which are (i) the molecular heat capacity of a solid compound which is the sum of the atomic heat capacities of the elements composing it, and (ii) the elements having atomic heat capacities lower than those required by the law of Dulong and Petit retain these lower values in their compounds. Also, there is a regular relationship between boiling points and the number of methylene (CH_2) groups present in the molecule.

Kraft Process

The Kraft chemical recovery process is a mature, effective technology that provides for recycling of the pulping chemicals, efficient generation of steam and electrical power from the fuel value of the black liquor, and effective disposal of dissolved wood substances. Thus:

Wood (lignin + fiber)	white liquor ($\text{NaOH} + \text{Na}_2\text{S}$)	black liquor (+ fiber)
--------------------------	---	---------------------------

In the process, which uses sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to pulp wood, approximately 50% w/w of the wood is dissolved, and together with the spent pulping chemicals, forms a liquid stream called weak black liquor. The weak black liquor is separated from the pulp by washing, and is sent to the recovery system, where the inorganic pulping chemicals are recovered for reuse, while the dissolved organics are used as a fuel to make steam and power.

The process has three main functions, which are (i) to minimize the environmental impact of waste material – the black liquor – from the pulping process, (ii) recycling the pulping chemicals, sodium hydroxide and sodium sulfide, NaOH and Na_2S ; and (iii) co-generating steam and power.

Landfill Classification

A landfill site is an area of land that has been specifically engineered to allow for the deposition of waste on to and into it. Municipal solid waste landfill sites are a large source of human-related methane *emissions* and, in some countries such as the United States, can account for up to 25% of these emissions. At the same time, methane emissions from landfills represent a lost opportunity to capture and use a significant energy resource.

Historically, a landfill has been called a dump or a midden and has been the most convenient method of waste disposal for millennia. Landfills may include internal waste disposal sites (where a producer of waste carries out their own waste disposal at the place of production) as well as sites used by many producers. Many landfills are also used for other waste management purposes, such as the temporary storage, consolidation and transfer, or processing of waste material (sorting, treatment, or recycling). A landfill also may refer to ground that has been filled in with soil and rocks instead of waste materials, so that it can be used for a specific purpose, such as for building houses.

Landfill sites are classified according to the type(s) of waste material contained therein, viz: (i) hazardous waste landfill site, (ii) sanitary landfill site, (iii) inert waste landfill site, and (iv) dump site (Table L-1). In the hazardous waste landfill site, waste disposal units are constructed to specific design criteria and which receive wastes meeting the local definition of hazardous waste. These landfills are generally constructed to be secure repositories for material that presents a serious hazard to human health, such as high-level radioactive waste. They are restricted, by permit or law, to the types of waste that they may handle (chemical vs. radioactive, liquid vs. dry). Double liner systems are the norm for hazardous waste landfills.

Table L-1 General classification of landfill sites.

Landfill type	Description
Dump	Also simply referred to as a landfill.
	Not engineered with the special protective measures required by sanitary landfills.
	Most common in rural, remote, and developing areas.
	Many jurisdictions prohibit the use of non-sanitary landfills for the disposal of municipal solid waste.
	Some jurisdictions that do allow dumps may require them to be constructed according to some engineering standard to mitigate the risk for environmental contamination, such as by limiting the slope, requiring compaction, or ensuring that the cell is high enough above the groundwater table.
Vegetation waste	Also known as yard waste and stump fill areas.
	Used to dispose of vegetation wastes.
	Generally unregulated prior to the 1980s.
	In areas where burning was prohibited, these areas were used by land developers to bury trees and brush cleared from land used for subdivisions and commercial developments.
Animal waste	An area where massive amounts of manure and, possibly, animal carcasses are disposed.
	As a result of the high organic content, methane production can be significant.

(Continued)

Table L-1 General classification of landfill sites. (*Continued*)

Landfill type	Description
	Decaying manure and carcasses will produce strong odors.
	Fires have occurred on some animal waste landfills, increasing health and safety concerns.
Inert waste	A waste disposal unit that receives wastes which are chemically and physically stable and do not undergo decomposition, such as sand, bricks, concrete, and gravel.
Sanitary	Normally refers to those where municipal solid waste is disposed of, as well as other wastes high in organic material
	Also called modern, engineered, or secure landfills.
	Usually have physical barriers such as liners and leachate collection systems, and procedures to protect the public from exposure to the disposed wastes. The term sanitary landfill.
Hazardous waste	Waste disposal units constructed to specific design criteria and which receive wastes meeting the local definition of hazardous waste.
	Generally constructed to be secure repositories for material that presents a serious hazard to human health, such as high-level radioactive waste.
	Restricted, by permit or law, to the types of waste that they may handle (chemical vs. radioactive, liquid vs. dry).
	Double liner systems are the norm for hazardous waste landfills.

A sanitary landfill site (also called modern, engineered, or secure landfills) usually has physical barriers such as liners and leachate collection systems, and procedures to protect the public from exposure to the disposed wastes. The term sanitary landfill normally refers to those where municipal solid waste is disposed of, as well as other wastes high in organic material. In some countries, all landfills are sanitary landfills.

The inert waste landfill site waste is used for receiving wastes which are chemically and physically stable and do not undergo decomposition, such as sand, bricks, concrete, or gravel.

The dump site: also simply called landfills; dumps are landfills that are not engineered with the special protective measures required by sanitary landfills. They are most common in rural, remote, and developing areas. Many jurisdictions prohibit the use of non-sanitary landfills for the disposal of municipal solid waste. Other jurisdictions that do allow dumps may require them to be constructed according to some engineering standard to mitigate the risk for environmental contamination, such as by limiting the slope, requiring compaction, or ensuring that the cell is high enough above the groundwater table.

Whatever the classification, the landfill site should be designed in such fashion that there is minimal harm to the environment and that the land may be restored in some way after the period of waste disposal. Despite its connotations as an out of sight, out of mind solution, landfill is a well-used method of waste management that is applied to the majority of solid wastes in many countries and can be used as a source for biogas.

The production of alternate fuels from landfill gas is an emerging area. Landfill gas has been successfully delivered to the natural gas pipeline system as both a high-Btu and medium-Btu fuel. Landfill gas has also been converted to vehicle fuel in the form of compressed natural gas (CNG), with a number of liquefied natural gas (LNG), and can also be used for methanol production.

Most modern landfill sites are engineered to contain liquid leachate or landfill gas produced by decomposing organic waste, even to the point of requiring a minimum of one landfill liner. This consists of a layer of compacted clay with a minimum required thickness and a maximum allowable hydraulic conductivity. A deep geological repository of high-level radioactive waste is not generally classified as a landfill site.

Municipal solid waste contains significant portions of organic materials that produce a variety of gaseous products when dumped, compacted, and covered in landfills. Anaerobic bacteria thrive in the oxygen-free environment, resulting in the decomposition of the organic materials and the production of primarily carbon dioxide and methane.

Carbon dioxide is likely to leach out of the landfill because it is soluble in water. Methane, on the other hand, which is less soluble in water and lighter than air, is likely to migrate out of the landfill. Landfill gas energy facilities capture the methane (the principal component of natural gas) and combust it for energy.

However, not all landfills are capable of producing landfill gas that is usable as an energy gas. Gas production is dependent upon the composition of the waste in the landfill, and this, in turn, dictates the classification of the landfill.

See also: Biogas, Landfill Gas, Waste, Waste-To-Energy.

Landfill Gas

Landfill gas (LFG, sometimes referred to under the collective groups known as biogas) is not the same as natural gas or methane; each has a separate identity, and the names should not be used interchangeably. Landfill gas is produced by the microbial decomposition of landfilled waste in an oxygen-free (anaerobic) atmosphere. This generally occurs under semi-controlled conditions in a landfill; its constituents depend on the composition and age of the waste.

Landfill gas is, in fact, a fuel gas that is a by-product of current landfilling practices and hence occurs only after municipal solid waste has been sent for disposal to a landfill site. The anaerobic digestion of the buried solid organic waste produces the landfill gas naturally, as the bacterial decomposition of the organic matter continues over time. In the long run, as the use of landfills necessarily dwindle, landfill gas will disappear as a resource. It is thus of an inherently transient nature, but will be covered here as many examples of landfill gas plants exist.

The term landfill methane is deceiving as it may seem to imply (incorrectly) that landfill gas is simply methane. Landfill gas is produced by the microbial decomposition of landfilled waste in an oxygen-free (anaerobic) atmosphere. The gas is approximately 65% v/v methane and 35% v/v carbon dioxide as well as traces of other constituents (Table L-2), but the composition of the gas does vary with age and the type of waste. The odor of landfill gas is associated with trace compounds such as hydrogen sulfide, mercaptans, and ethylene. On occasion, mercury and even radioactive contaminants such as tritium (radioactive hydrogen) have been found in landfill gas.

Table L-2 Typical constituents of landfill gas.*

Component	% v/v	Characteristics
Ammonia	0.1-1	Colorless gas with a pungent odor.
Carbon dioxide	40-60	Colorless, odorless, and slightly acidic.
Carbon monoxide	0.0-2	Colorless, odorless.
Hydrogen	0-0.2	Colorless, odorless, tasteless.
Methane	45-60	A naturally occurring gas; colorless and odorless.
Nitrogen	2-5	Colorless, odorless, and tasteless.
NMOCs**	0.01-0.6	Organic compounds excluding methane.
Oxygen	0.1-1	Colorless, odorless, tasteless.
Sulfides	0-1	Hydrogen sulfide, dimethyl sulfide, mercaptans

*Listed alphabetically rather than by occurrence.

**Non-methane organic compounds.

The rate and duration of gas production depends on the nature of the waste and oxygen availability. Some sites may continue gassing for over 50 years. The gas can move or migrate in any direction within the site, depending on the permeability of the waste layers. It can also migrate off-site if measures are not taken to prevent it. One indication that gas is escaping from the site and venting through the ground outside is the presence of yellow and dying vegetation.

The length of time and amount of gas that is available from a landfill site is specific to the type of waste, moisture content, temperature, acidity, and the design of the site. As the diagram above shows, gas is drawn up from vertical or horizontal wells through a system of pipes. At this stage, the gas is usually warm and saturated with moisture.

The extraction pipes contain condensate traps and are laid at an angle so that as the gas cools, the moisture does not hinder the flow of the gas. The condition of the gas is specific to what use it will be put to.

The rate and duration of gas production depends on the nature of the waste and oxygen availability. The gas can move or migrate in any direction within the site, depending on the permeability of the waste layers. It can also migrate off-site if measures are not taken to prevent it. One indication that gas is escaping from the site and venting through the ground outside is the presence of yellow and dying vegetation.

A main concern with landfill gas is the possibility of gas accumulation inside buildings constructed on or close to a landfill site. Protection of new buildings is usually achieved using a dual barrier approach: low permeability gas membrane to resist the passage of gas, and some form of ventilation/extraction system to disperse the gas safely to the atmosphere. The requirements for particular developments will be specified by the relevant planning authorities. Gas monitoring may also be a requirement and, if so, indicates that gas detectors must be installed at the most effective location.

Gas monitoring and control measures are the responsibility of the site operator, and the aim of gas control is to prevent migration off-site. This can be achieved by a gas barrier (lining of the excavation) combined with stone-filled vent trenches which can vent gas to atmosphere. Venting can also be carried out using borehole pipes spread throughout the site or at selected points where gas can be pumped to them through a gas drainage system inside the tip. If the quantity or quality (odor) of the gas is such that it requires destroying, a flare system may be adopted. Landfill gas can also be exploited for industrial use as fuel for heat or to produce electricity.

Collection

In order to use the landfill gas, it must first be collected from the landfill. A collection system usually consisting of vertical extraction wells gas pipeline, blower units, and possibly a flare to burn off gases safely is used. These collection wells are placed strategically throughout the landfill site. If the gas production is significant, each extraction well is connected to the main gas line, which carries the gas to a station; landfill operators can either sell the gas or use it for energy.

The gas is extracted from the landfill by means of a gas pump or a compressor leading the gas to a utilization plant by means of pressure in the transmission pipe. The connection of the single wells to the pump and utilization system can be done in different ways. The most common method, is to connect the wells to a main collection pipe which goes around on the landfill. The main problem with this system is the difficulty involved with the regulation of both the quality and quantity of the gas. Another problem is to find the location of leakiness when all the wells are connected in one big system. To save operation costs and to have good conditions for the workers, the best solution is to have single pipes from each well to a pump and regulation house.

Composition

The composition of landfill gas is variable (Table L-2), and the evolution rate of the gas from the landfill and the quantity of gas are dependent on a number of factors. These factors include (i) the composition of the waste, (ii) the age of waste, (iii) the presence of oxygen, (iv) the moisture content of the waste, (v) the temperature, (vi) the input rate of the waste, (vii) the ambient pH, (viii) the density of the waste density which is an indicator of whether is waste is tightly packed or loosely packed), and (ix) the management strategy/strategies of the site.

The composition of the waste, especially the amount of organic waste present in a landfill, determines the level of bacterial activity and the degree of bacterial decomposition. Some types of organic waste contain nutrients, such as sodium, potassium, calcium, and magnesium, which help bacteria thrive. When these nutrients are present, landfill gas production increases. Alternatively, some wastes contain compounds that harm bacteria, causing less gas to be produced. For example, methane-producing bacteria can be inhibited when waste has high salt concentrations.

The presence of oxygen in a landfill also dictates the mode of decomposing. Only when oxygen is used up will bacteria begin to produce methane. The more oxygen present in a landfill, the longer aerobic bacteria can decompose waste during the first phase of the decomposition. If waste is loosely buried or frequently disturbed, more oxygen is available, so that oxygen-dependent bacteria live longer and produce carbon dioxide and water for longer periods. If the waste is highly compacted, however, methane production will begin earlier as the aerobic bacteria are replaced by

methane-producing anaerobic bacteria in the third phase of the decomposition. Methane gas starts to be produced by the anaerobic bacteria only when the oxygen in the landfill is used up by the aerobic bacteria; therefore, any oxygen remaining in the landfill will slow methane production. Barometric highs will tend to introduce atmospheric oxygen into surface soils in shallow portions of a landfill, possibly altering bacterial activity. In this scenario, waste in the fourth phase of the decomposition, for example, might briefly revert to Phase I until all the oxygen is used up again.

The presence of water in a landfill increases gas production because moisture encourages bacterial growth and transports nutrients and bacteria to all areas within a landfill. A moisture content of 40% or higher, based on wet weight of waste, promotes maximum gas production (e.g., in a capped landfill). Waste compaction slows gas production because it increases the density of the landfill contents, decreasing the rate at which water can infiltrate the waste. The rate of gas production is higher if heavy rainfall and/or permeable landfill covers introduce additional water into a landfill.

Temperature effects can vary, but, generally, warm temperatures increase bacterial activity, which in turn increases the rate of landfill gas production. Colder temperatures inhibit bacterial activity. Typically, bacterial activity drops off dramatically below 10°C (50°F). Weather changes have a far greater effect on gas production in shallow landfills because the bacteria are not as insulated against temperature changes as compared to deep landfills where a thick layer of soil covers the waste. A capped landfill usually maintains a stable temperature, maximizing gas production. Bacterial activity releases heat, stabilizing the temperature of a landfill between 77°F and 113°F, although temperatures up to 158°F have been noted. Temperature increases also promote volatilization and chemical reactions. As a general rule, emissions of organic compounds other than methane double with every 10°C (18°F) increase in temperature.

The age of refuse is also an important factor – recently buried waste will produce more gas than older waste. Landfills usually produce appreciable amounts of gas within 1 to 3 years. Peak gas production usually occurs 5 to 7 years after wastes are dumped. Almost all gas is produced within 20 years after waste is dumped; however, small quantities of gas may continue to be emitted from a landfill for 50 or more years. A low-methane yield scenario, however, estimates that slowly decomposing waste will produce methane after 5 years and continue emitting gas over a 40-year period. Different portions of the landfill might be in different phases of the decomposition process at the same time, depending on when the waste was originally placed in each area. The amount of organic material in the waste is an important factor in how long gas production lasts.

In addition, the pressure of the gas is also affected by (i) the rate of landfill gas evolution since a higher rate of gas evolution will result in an increase in the pressure of the landfill, (ii) the permeability of the surrounding waste types and or strata (rock type) since more permeable waste and or rock types will result in lower pressures as they will allow the landfill gas to migrate further than less permeable types, and (iii) variations in leachate levels since an increase in leachate levels lead to a decrease in volume and thus the pressure within the landfill increases.

See also: Biogas, Landfill, Waste, Waste-To-Energy.

Extraction

Landfill gas is extracted from landfills using a series of wells and, if necessary, a blower/flare (or vacuum) system.

The recovery system is constructed so that there is no leak of gas to the surrounding land or air. This methane and carbon dioxide mixture can be used in the same combustion process discussed previously. The generation equipment is usually contained within the same area as the extraction plant. This site is usually away from urban sites due to safety reasons and amenity.

This system directs the collected gas to a central point where it can be processed and treated depending upon the ultimate use for the gas. From this point, the gas can be simply flared or used to generate electricity, replace fossil fuels in industrial and manufacturing operations, fuel greenhouse operations, or be upgraded to pipeline quality gas.

A landfill gas extraction facility will typically consist of gas well fields, a gas processing plant, and a gas delivery pipeline to the customer. This will allow (i) recovery of the crude gas being generated within the landfill, (ii) the ability to process the gas to produce medium Btu gas – approximately 500 Btu/ft³, and (iii) delivery to a pipeline of specification gas.

At the facility, the gas is drawn from the wells and sent to a main collection header and thence to the processing plant. Vapor-liquid separators are used to separate water and any liquid condensate from the gas. The condensate is

usually a mixture of hydrocarbon derivatives that resembles contaminated gasoline or kerosene. Further vapor contaminant removal is accomplished by solvent scrubbing. The crude gas is compressed and then cooled and scrubbed by countercurrent solvent flow.

Formation

Most landfill gas is produced by bacterial decomposition, which occurs when organic waste is broken down by bacteria naturally present in the waste and in the soil used to cover the landfill. Organic wastes include food, garden waste, street sweepings, textiles, and wood and paper products.

Bacteria decompose organic waste in four phases, and the composition of the gas changes during each phase. Bacteria decompose landfill waste in four phases. The composition of the gas produced changes with each of the four phases of decomposition. Landfills often accept waste over a 20- to 30-year period, so waste in a landfill may be undergoing several phases of decomposition at once. This means that older waste in one area might be in a different phase of decomposition than more recently buried waste in another area.

During the first phase of decomposition, aerobic bacteria consume oxygen while breaking down the long molecular chains of complex carbohydrates, proteins, and lipids that comprise organic waste. The primary by-product of this process is carbon dioxide. Nitrogen content is high at the beginning of this phase, but declines as the landfill moves through the four phases. The chemistry of this first phase continues until the available oxygen is depleted. This phase can last for days or months, depending on how much oxygen is present when the waste is disposed in the landfill. Oxygen levels will vary according to factors such as how loose or compressed the waste was when it was buried.

The second phase of Phase II decomposition starts after the oxygen in the landfill has been used up. Using an anaerobic process (a process that does not require oxygen), bacteria convert compounds created by aerobic bacteria into acetic, lactic, and formic acids and alcohols such as methanol and ethanol. The landfill becomes highly acidic. As the acids mix with the moisture present in the landfill, they cause certain nutrients to dissolve, making nitrogen and phosphorus available to the increasingly diverse species of bacteria in the landfill. The gaseous by-products of these processes are carbon dioxide and hydrogen. If the landfill is disturbed or if oxygen is somehow introduced into the landfill, microbial processes will return to the first phase.

The third phase of decomposition starts when certain kinds of anaerobic bacteria consume the organic acids produced in second phase and form acetate, an organic acid. This process causes the landfill to become a more neutral environment in which methane-producing bacteria begin to establish themselves. Methane- and acid-producing bacteria have a symbiotic, or mutually beneficial, relationship. Acid-producing bacteria create compounds for the methanogenic bacteria to consume. Methanogenic bacteria consume the carbon dioxide and acetate, too much of which would be toxic to the acid-producing bacteria.

The final phases of the decomposition begin when both the composition and production rates of landfill gas remain relatively constant. At this stage, the landfill gas usually contains approximately 45% to 60% methane by volume, 40% to 60% carbon dioxide, and 2% to 9% other gases, such as sulfides. Gas is produced at a stable rate during this final phase – typically for approximately 20 years. However, gas will continue to be emitted for 50 or more years after the waste is placed in the landfill. Gas production might last longer, for example, if greater amounts of organics are present in the waste, such as at a landfill receiving higher than average amounts of domestic animal waste.

Several factors affect the composition of landfill gas, and these are (i) composition of the waste, (ii) oxygen in the landfill, (iii) moisture content of the waste/landfill, (iv) temperature, and (v) time of burial of the waste in the landfill.

In terms of waste composition, the more organic waste present in a landfill, the more landfill gas is produced by bacterial decomposition. Some types of organic waste contain nutrients, such as sodium, potassium, calcium, and magnesium, which help bacteria thrive. When these nutrients are present, landfill gas production increases. Alternatively, some wastes contain compounds that harm bacteria, causing less gas to be produced. For example, methane-producing bacteria can be inhibited when waste has high salt concentrations.

Only when oxygen is used up will bacteria begin to produce methane. The more oxygen present in a landfill, the longer aerobic bacteria can decompose waste in Phase I. If waste is loosely buried or frequently disturbed, more oxygen is available, so that oxygen-dependent bacteria live longer and produce carbon dioxide and water for longer periods. If the waste is highly compacted, however, methane production will begin earlier as the aerobic bacteria are replaced by methane-producing anaerobic bacteria in Phase III. Methane gas starts to be produced by the anaerobic bacteria only when the oxygen in the landfill is used up by the aerobic bacteria; therefore, any oxygen remaining in

the landfill will slow methane production. Barometric highs will tend to introduce atmospheric oxygen into surface soils in shallow portions of a landfill, possibly altering bacterial activity. In this scenario, waste in Phase IV, for example, might briefly revert to Phase I until all the oxygen is used up again.

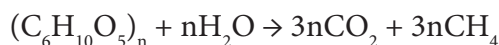
The presence of water in a landfill increases gas production because moisture encourages bacterial growth and transports nutrients and bacteria to all areas within a landfill. A moisture content of 40% or higher, based on wet weight of waste, promotes maximum gas production (e.g., in a capped landfill). Waste compaction slows gas production because it increases the density of the landfill contents, decreasing the rate at which water can infiltrate the waste. The rate of gas production is higher if heavy rainfall and/or permeable landfill covers introduce additional water into a landfill.

A slightly elevated temperature increases bacterial activity, which in turn increases the rate of landfill gas production. Colder temperatures inhibit bacterial activity. Typically, bacterial activity drops off dramatically below 10°C (50°F). Weather changes have a far greater effect on gas production in shallow landfills. This is because the bacteria are not as insulated against temperature changes as compared to deep landfills where a thick layer of soil covers the waste. A capped landfill usually maintains a stable temperature, maximizing gas production. Bacterial activity releases heat, stabilizing the temperature of a landfill between 25 and 45°C (77 and 113°F), although temperatures up to 70°C (158°F) have been noted. Temperature increases also promote volatilization and chemical reactions. As a general rule, emissions of the non-methane organic compounds double with every 10°C (18°F) increase in temperature.

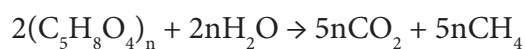
The time of burial is also a factor in gas production – for example, waste that has recently been buried will produce more gas than older waste. Landfills usually produce appreciable amounts of gas within 1 to 3 years. Peak gas production usually occurs 5 to 7 years after wastes are dumped. Almost all gas is produced within 20 years after waste is dumped; however, small quantities of gas may continue to be emitted from a landfill for 50 or more years. A low-methane yield scenario, however, estimates that slowly decomposing waste will produce methane after 5 years and continue emitting gas over a 40-year period. Different portions of the landfill might be in different phases of the decomposition process at the same time, depending on when the waste was originally placed in each area. The amount of organic material in the waste is an important factor in how long gas production lasts.

There are five major reaction processes involved with different microorganisms involved at each stage and, although much more complex, the chemistry occurring at landfill sites is generally represented in the simplest form as the decomposition of cellulose and hemicellulose.

For cellulose:



For hemicellulose:



The reactions actually occur in stages, and cellulose and hemicellulose are not the only starting materials.

The initial stage of organic decomposition occurs during the placement of the waste in the landfill and for the period of time after, when oxygen is available within the waste. There, chemical processes are initiated and facilitated by the presence of aerobic micro-biota which metabolize a fraction of the organic waste to produce simpler hydrocarbon derivatives, water, carbon dioxide, and, as this is an exothermic reaction, heat (the heat generated can raise the temperature of the waste to up to 70 to 90°C (160 to 195°F); however, compacted waste achieves lower temperatures due to the reduced availability of oxygen).

In these reactions, water and carbon dioxide are produced in the greatest concentrations. The carbon dioxide can dissolve in the water, forming a leachate that is rich in carbonic acid, which, in turn, lowers the pH of the surroundings. This stage generally lasts for a matter of days or weeks, depending on the amount of oxygen that is available within the waste.

The removal of oxygen during the hydrolysis and aerobic degradation facilitates a change in conditions from aerobic (oxygen present) to anaerobic (oxygen absent). Thus the majority of microbiota found within the waste change to anaerobic species. Carbohydrates are hydrolyzed (a chemical process in which a molecule is split into two parts

by the addition of a water molecule) to sugars, which are then further decomposed to form carbon dioxide, hydrogen, ammonia, and organic acids. Proteins decompose via removal of an amino (NH_2) group to form ammonia, carboxylic acids, and carbon dioxide. The leachate that is produced at this stage contains ammoniacal nitrogen in high concentration. Acetic acid is the main organic acid formed, but propionic, butyric, lactic and formic acids, and acid derivative products are also produced, and their formation is affected by the composition of the initial waste material. The temperatures in the landfill drop to between 30 and 50°C (86 and 122°F). Gas composition may rise to levels of up to 80% carbon dioxide and 20% hydrogen.

In the acetogenesis stage, anaerobic conditions are still present and the organic acids that were formed in the hydrolysis and fermentation stage are now converted, via specific microorganisms to acetic acid, acetic acid derivatives, carbon dioxide, and hydrogen. Other microorganisms convert carbohydrates directly to acetic acid in the presence of carbon dioxide and nitrogen. Hydrogen and carbon dioxide levels begin to diminish toward the end of this stage, with the lower hydrogen concentrations promoting the methane-generating microorganisms (methanogens), which subsequently generate methane and carbon dioxide from the organic acids and their derivatives generated in the earlier stages.

The methanogenesis stage encompasses the main processes that lead to the production of landfill gas. At this point, the chemical processes involved are comparatively slow and can take many years to complete. Oxygen-depleted, anaerobic conditions still remain as in the previous two stages. Low levels of hydrogen are required to promote the methanogenic organisms, which generate carbon dioxide and methane from the organic acids and their derivatives such as acetate derivatives and formate derivatives that are formed in the earlier stages. Methane generation may also occur from the direct conversion of hydrogen and carbon dioxide (via microorganisms) in to methane and water: Hydrogen concentrations, produced during Stages 2 and 3, therefore fall to low levels during this fourth stage.

Oxidation processes mark the final stage of the reactions involved in the biodegradation of waste. As the acids are used up in the production of landfill gas, new aerobic microorganisms slowly replace the anaerobic forms and re-introduce oxygen to the region. Microorganisms that convert methane to carbon dioxide and water may also become established.

There are also inorganic reactions involving inorganic waste which involve (i). sulfate-containing materials and (ii) heavy metals. In the former case, plaster board (in this case, the sulfate is present in the form of gypsum) will be reduced under anaerobic, oxygen-deficient, conditions to produce a metal sulfide (via association with free metal ions). Under acidic conditions, the sulfate will be released as hydrogen sulfide (H_2S), which has the potential to present a serious hazard. The gas is toxic and can cause respiratory arrest if large concentrations are inhaled. Also, at concentrations above 100 ppm, the ability of a person to detect the gas is affected by rapid temporary paralysis of the olfactory nerves in the nose, leading to a loss of the sense of smell. This unusual property makes it extremely dangerous to rely totally on the sense of smell to warn of the presence of hydrogen sulfide.

Reduced sulfate, in the form of sulfide, will react with heavy metals (see above), producing a metal sulfide, which is comparatively immobile. Other insoluble salts such as metal carbonates may also be formed. Although these are potential pollutants, their immobility reduces their potential to migrate out of the landfill site boundary.

See also: Landfill, Landfill Gas, Waste.

Migration

Once gases are produced under the landfill surface, they generally move away from the landfill. Gases tend to expand and fill the available space, so that they move or migrate through the limited pore spaces within the refuse and soils covering of the landfill. The tendency of some landfill gases, such as methane, that is lighter than air, is to move upward, usually through the landfill surface. However, of the hydrocarbon derivatives, methane is the only one that is lighter than air. Higher-molecular-weight hydrocarbons such as ethane, propane, and butane are denser than air and may collect in pockets rather than migrate with the methane. This can cause problems when pockets are suddenly opened to the air (for example during landfill mining), and the flammability limit or flash point of the collected gas is reached.

In addition to the density phenomenon, upward movement of landfill gas can be inhibited by densely compacted waste or landfill cover material (e.g., by daily soil cover and caps). When upward movement is inhibited, the gas tends to migrate horizontally to other areas within the landfill or to areas outside the landfill, where it can resume its upward path. Basically, the gases follow the path of least resistance. Some gases, such as carbon dioxide, are denser

than air and will collect in subsurface areas, such as utility corridors. Three main factors influence the migration of landfill gases: diffusion (concentration), pressure, and permeability.

Diffusion is the natural tendency of a gas to reach a uniform concentration in a given space, whether it is a room or the atmosphere of the Earth. Gases in a landfill move from areas of high gas concentrations to areas with lower gas concentrations. Because gas concentrations are generally higher in the landfill than in the surrounding areas, landfill gases diffuse out of the landfill to the surrounding areas with lower gas concentrations.

Gases accumulating in a landfill create areas of high pressure in which gas movement is restricted by compacted refuse or soil covers and areas of low pressure in which gas movement is unrestricted. The variation in pressure throughout the landfill results in gases moving from areas of high pressure to areas of low pressure. Movement of gases from areas of high pressure to areas of lower pressure is known as convection. As more gases are generated, the pressure in the landfill increases, usually causing subsurface pressures in the landfill to be higher than either the atmospheric pressure or indoor air pressure. When pressure in the landfill is higher, gases tend to move to ambient or indoor air.

Gases will also migrate according to where the pathways of least resistance occur. Permeability is a measure of how well gases and liquids flow through connected spaces or pores in refuse and soils. Dry, sandy soils are highly permeable (many connected pore spaces), while moist clay tends to be much less permeable (fewer connected pore spaces). Gases tend to move through areas of high permeability (e.g., areas of sand or gravel) rather than through areas of low permeability (e.g., areas of clay or silt). Landfill covers are often made of low-permeability soils, such as clay. Gases in a covered landfill, therefore, may be more likely to move horizontally than vertically.

The direction, speed, and distance of landfill gas migration depend on a number of factors, such as (i) landfill cover, (ii) natural and man-made (anthropogenic) pathways, (iii) wind speed and direction, (iv) moisture, (v) groundwater levels, (vi) temperature, and (vii) gas pressure and barometric pressure.

If the landfill cover consists of relatively permeable material, such as gravel or sand, then gas will likely migrate up through the landfill cover. If the landfill cover consists of silts and clays, it is not very permeable; gas will then tend to migrate horizontally underground. If one area of the landfill is more permeable than the rest, gas will migrate through that area.

Drains, trenches, and buried utility corridors (such as tunnels and pipelines) can act as conduits for gas movement. The natural geology often provides underground pathways, such as fractured rock, porous soil, and buried stream channels, where the gas can migrate.

Wind speed and direction influence the fate of landfill gas naturally vented into the air at the landfill surface. The wind dilutes the gas with fresh air as it moves it to areas beyond the landfill. Wind speed and direction determine the concentration of the gas in the air, which can vary greatly from day to day, even hour by hour. In the early morning, for example, winds tend to be gentle and provide the least dilution and dispersion of the gas to other areas.

Wet surface soil conditions may prevent landfill gas from migrating through the top of the landfill into the air above. Rain and moisture may also seep into the pore spaces in the landfill and “push out” gases in these spaces. Water in the form of groundwater also influences gas movement. Variations in the groundwater table such as the water table is rising into an area will force the landfill gas upward.

Increases in temperature stimulate gas particle movement, tending also to increase gas diffusion, so that landfill gas might spread more quickly in warmer conditions. The landfill generally maintains a stable temperature; freezing and thawing cycles can cause the soil surface to crack, causing landfill gas to migrate in an upward direction and/or in a horizontal direction. Frozen soil over the landfill may provide a physical barrier to upward landfill gas migration, causing the gas to migrate further from the landfill horizontally through soil.

The difference between the soil gas pressure and barometric pressure allows gas to move either vertically or laterally, depending on whether the barometric pressure is higher or lower than the soil gas pressure. When the barometric pressure is falling, landfill gas will tend to migrate out of the landfill into surrounding areas. As barometric pressure rises, gas may be retained in the landfill temporarily as new pressure balances are established.

Monitoring

Landfill gas monitoring is the process by which gases that are released from landfills are electronically monitored.

Landfill gas production results from chemical reactions and microbes acting upon the waste as they begin to break down the waste. However, due to the constant production of landfill gas, pressure increases within the landfill provoke its release into the atmosphere and there is a clear need to monitor gas produced by landfills.

Techniques for monitoring of landfill gas include: (i) surface monitoring is used to check the integrity of caps on waste; this technique may give preliminary indications of gas migration off-site, (ii) 2. subsurface monitoring (gas probes) is used to enable point source monitoring of gas concentrations in the local environment around the probe; the monitoring system may contain a single probe or multiple probes (at different depths) at a single point; probes typically form a ring around a landfill, and the distance between probes varies (based upon several factors) and rarely exceeds 1,000 feet, (iii) excavated trenches and pits backfilled around standpipes provides means of measuring gas concentrations in shallow sites, (iv) gas monitoring boreholes or wells is the preferred method for measuring gas concentrations and sometimes flow rates both on and off site, (v) ambient air samplers are used to sample the air up-wind and down-wind of a landfill, over the period of several hours; samples are taken in special plastic bags or steel canisters and analyzed at a laboratory; when a landfill is situated in a location where the wind direction changes from day to night (such as near to a coastline), a 24-hour sampling period may be broken into day and night components, and (vi) the use of leachate wells may be used for gas monitoring but are not comparable with, or substitutes for specially designed gas monitoring points.

Power Generation

The gas generated in landfills can be tapped after the completion of the landfill, and when burnt as fuel has a calorific value approximately half that of natural gas. This is due to the fact that there is only approximately 60% v/v combustible methane in the gas (Table L-2). Generating electricity from landfill gas is clearly a better sustainable solution than merely trapping and not using it in any productive manner. It is a resource that should be employed. There is the added bonus for the site operators of extra generated financial revenue from the electricity sales. However, all of the environmental burdens still apply. The only offset is where electricity generation by non-renewable sources can be reduced.

Large municipal or industrial landfills produce gas that can be tapped to generate electricity. Microorganisms that live in organic materials such as food wastes, paper, or yard clippings cause these materials to decompose. This produces landfill gas, typically comprised of approximately 60% v/v methane and approximately 40% v/v carbon dioxide.

Landfill gas is collected from landfills by drilling "wells" into the landfills, and collecting the gases through pipes. Once the landfill gas is processed, it can be combined with natural gas to fuel conventional combustion turbines or used to fuel small combustion or combined cycle turbines. Landfill gas may also be used in fuel cell technologies, which use chemical reactions to create electricity, and are much more efficient than combustion turbines. However, use of the gas produced by landfills may reduce the harmful environmental impacts that would otherwise result from landfill operations. Landfill gas electricity generation offers major air quality benefits where landfills already exist or where the decision to build the landfill has already been made. Landfill gas power plants reduce methane emissions, a global climate change agent with twenty-three times the negative impact of carbon dioxide.

A landfill gas power plant burns methane that would otherwise be released into the atmosphere or burned off in a flaring process. Methane is a highly potent agent of global climate change, having approximately 23 times the negative impact on a pound-by-pound basis as carbon dioxide. Landfill gas combustion produces some carbon dioxide, but the impact of these emissions on global climate change is offset many times over by the methane emission reductions.

Landfill gas generators produce nitrogen oxides emissions that vary widely from one site to another, depending on the type of generator and the extent to which steps have been taken to minimize such emissions. Combustion of landfill gas can also result in the release of organic compounds and trace amounts of toxic materials, including mercury and dioxins, although such releases are at levels lower than if the landfill gas is flared.

There are few water impacts associated with landfill gas power plants. Unlike other power plants that rely upon water for cooling, landfill gas power plants are small, and therefore pollution discharges into local lakes or streams are typically quite small.

Pretreatment

After collecting the gas from the wells, the methane-rich gas is flared or pre-treated before being used in an energy recovery system. Treatment requirements depend on the end use application. When the landfill gas is required for energy or any other use, a rigorous pre-treatment of the gas is required.

Treatment systems can be divided into primary treatment processing and secondary treatment processing. Most primary processing systems include de-watering and filtration to remove moisture and particulates. Dewatering can be as simple as physical removal of free water or condensate in the landfill gas. However, it is common to remove water vapor using gas cooling and compression.

Secondary treatment systems are designed to provide much greater gas cleaning than primary gas cleaning systems. A large portion of the landfill gas consists of carbon dioxide which is non-combustible and therefore reduces the calorific value of the gas. Furthermore, in the presence of ambient moisture, acid gases produce acid rain, which is a well-known global environmental menace. The various gas cleaning systems may employ multiple cleanup processes depending on the gas specifications of the end use. Such processes include both physical and chemical treatments. The most common technologies used for secondary treatment are absorption and adsorption.

The removal of these toxic compounds can be done through dry or wet scrubbing processes. The scrubbing process is an operation in which one or more components of a gas stream are selectively absorbed into an absorbent. The term scrubbing is used interchangeably with “absorption” when describing this process. In wet scrubbing, a relatively non-volatile liquid is used as the absorbent. In dry scrubbing, a dry powder or semidry slurry are possible absorbents. Adsorption involves the binding of a particle to the surface. In this case, the surface is usually carbon or silica gel. There also exist advanced treatment technologies that remove carbon dioxide, non-methane organic compounds (NMOCs), and a variety of other contaminants in gas streams to produce a high-Btu gas.

Landfill gas can be upgraded to natural gas quality so that it can be used in the existing natural gas distribution network. One of the indices used to evaluate the quality of gas for comparative use is the Wobbe Index. The Wobbe Index allows for the comparison of the volumetric energy content of different gas fuels at different temperatures. Gas streams can possess varying heating values and relative densities but have the same Wobbe Index, *i.e.*, they will deliver the same heat and yield the same performance for a given process.

The upgrading process involves a series of complex processes which will result in the removal of elements such as, hydrogen sulfide, carbon dioxide, heavy hydrocarbon, siloxanes, nitrogen, and oxygen. Though the process used to remove such gasses is not new when applied to landfill gas, it may not be a cost-effective option. Upgraded landfill gas can also be used as chemical feedstock in the process industry such as in the production of diesel fuel and methanol. The process involves the upgrading of the landfill gas to chemical feedstock quality, hence rendering this option economically unattractive.

Production

Most landfill gas is produced by bacterial decomposition, which occurs when organic waste is broken down by bacteria naturally present in the waste and in the soil used to cover the landfill. Organic wastes include food, garden waste, street sweepings, textiles, and wood and paper products. Bacteria decompose organic waste in *four phases*, and the composition of the gas changes during each phase.

During the first phase of decomposition, aerobic bacteria (bacteria that live only in the presence of oxygen) consume oxygen while breaking down the long molecular chains of complex carbohydrates, proteins, and lipids that comprise organic waste. The primary by-product of this process is carbon dioxide. Nitrogen content is high at the beginning of this phase, but declines as the landfill moves through the four phases. The chemistry of this first phase continues until the available oxygen is depleted. This phase can last for days or months, depending on how much oxygen is present when the waste is disposed in the landfill. Oxygen levels will vary according to factors such as how loose or compressed the waste was when it was buried.

The *second phase* commences after the oxygen in the landfill has been consumed and is followed by the anaerobic phase (a process that does not require oxygen) in which the bacteria convert compounds created by aerobic bacteria into acetic acid, lactic acid, formic acid, and alcohol derivatives such as methanol and ethanol. The landfill becomes highly acidic and, as the acid derivatives mix with the moisture present in the landfill, the acids cause certain nutrients to dissolve, making nitrogen and phosphorus available to the increasingly diverse species of bacteria in the landfill. The gaseous by-products of these processes are carbon dioxide and hydrogen. If the landfill is disturbed or if oxygen is introduced into the landfill, microbial processes return those chemical processes typical of the *first phase* of decomposition.

The *third phase* commences when certain kinds of anaerobic bacteria consume the organic acids produced in the *second phase* and form acetate, an organic acid. This process causes the landfill to become a more neutral

environment in which methane-producing bacteria begin to establish themselves. The methane-producing and the acid-producing bacteria have a symbiotic relationship insofar as the acid-producing bacteria create compounds for the methanogenic bacteria to consume. Also, the methanogenic bacteria consume the carbon dioxide and acetate, too much of which would be toxic to the acid-producing bacteria.

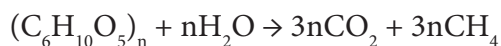
The *fourth phase* of decomposition begins when both the composition and production rates of landfill gas remain relatively constant. The gas produced in this phase usually contains approximately 45% to 60% methane by volume, 40% to 60% carbon dioxide, and 2% to 9% other gases, such as sulfides. Gas is produced at a stable rate, typically for approximately 20 years. However, gas will continue to be emitted for 50 or more years after the waste is placed in the landfill (Crawford and Smith 1985). Gas production might last longer, for example, if greater amounts of organics are present in the waste, such as at a landfill receiving higher than average amounts of domestic animal waste.

As might be anticipated from the above paragraphs, there are many reactions that occur among the array of waste that is sent to landfill. Of the wastes that are disposed to landfill, municipal wastes are likely to play the greatest role in chemical reactions, with perhaps some arising as a result of hazardous waste. However, as the name suggests, inert wastes are chemically un-reactive. The majority of reactions occur as a result of the biodegradation, or breakdown, of organic material via microbial activity, but chemical interactions can also be seen to exist in the case of inorganic materials.

Many of the biochemical reactions in landfill sites occur as a result of the presence of the reactive, organic wastes which account for more than half of the typical household waste (Hester and Harrison, 2002 page 29). There are five major reaction processes involved with different microorganisms involved at each stage.

Although much more complex, the chemistry occurring at landfill sites is generally represented in the simplest form as the decomposition of cellulose and hemicellulose.

Cellulose:



Hemicellulose:



The reactions actually occur in stages, and cellulose (Section 2.1) and hemicellulose are not the only starting materials.

While the reactions described above are organic chemical reactions, there are also inorganic chemical reactions by which landfill gas is produced.

There are two prominent examples of reactions involving inorganic waste which are (i) sulfate-containing materials and (ii) heavy metals (Hester and Harrison 1995). In the former case, plaster board (in this case, the sulfate is present in the form of gypsum) will be reduced under anaerobic, oxygen-deficient, conditions to produce a metal sulfide (via association with free metal ions). Under acidic conditions, the sulfate will be released as hydrogen sulfide (H_2S), which has the potential to present a serious hazard. The gas is toxic and can cause respiratory arrest if large concentrations are inhaled. Also, at concentrations above 100 ppm, the human ability to detect the gas is affected by rapid temporary paralysis of the olfactory nerves in the nose, leading to a loss of the sense of smell which makes it extremely dangerous to rely totally on the sense of smell to warn of the presence of hydrogen sulfide.

Reduced sulfate, in the form of sulfide, will react with heavy metals (see above), producing a metal sulfide, which is comparatively immobile. Other insoluble salts such as metal carbonates may also be formed. Although these are potential pollutants, their immobility reduces their potential to migrate out of the landfill site boundary.

Recovery and Use

Landfill gas recovery is the process by which methane is collected from solid waste deposited in a landfill. Instead of escaping into the air, landfill gas can be captured, converted, and used as a renewable energy resource. Using landfill gas helps to reduce odors and other hazards associated with gas emissions.

Thus, instead of escaping into the air, landfill gas can be captured, converted, and used as a renewable energy resource. Using landfill gas helps to reduce odors and other hazards associated with gas emissions, and prevents methane from migrating into the atmosphere and contributing to local smog and global climate change. In addition, landfill gas energy projects generate revenue and create jobs in the community and beyond.

Landfill gas (LFG) is extracted from landfills using a series of wells and a blower/flare (or vacuum) system which is used to direct the collected gas to a central point where it can be processed and treated depending upon the ultimate use for the gas. From this point, the gas can be flared or beneficially used in a landfill gas energy project. Thus, the four main steps in the process are:

Landfill with waste in place → gas extraction wells
 Gas extraction wells → primary processing
 Primary processing → additional treatment
 Additional treatment → generation of alternative energy

There are many options available for converting LFG into energy. Different types of LFG energy projects are grouped below into three broad categories – (i) electricity generation, (ii) direct use of medium-Btu gas, and (iii) renewable natural gas.

A variety of technologies, including reciprocating internal combustion engines, turbines, microturbines, and fuel cells, can be used to generate electricity for onsite use and/or sale to the grid. The reciprocating engine is the most commonly used conversion technology for landfill gas electricity applications because of its relatively low cost, high efficiency, and size ranges that complement the gas output of many landfills. Gas turbines are typically used in larger landfill gas energy projects, while microturbines are generally used for smaller landfill gas volumes and in niche applications.

Cogeneration, also known as combined heat and power (CHP), projects use landfill gas to generate both electricity and thermal energy, usually in the form of steam or hot water. Several cogeneration projects using engines or turbines have been installed at industrial, commercial, and institutional operations, using engines or turbines. The efficiency gains of capturing the thermal energy in addition to electricity generation can make this project type an attractive option.

Direct use of landfill gas to offset the use of another fuel (for example, natural gas, coal, or fuel oil) occurs as the gas can be used directly in a boiler, dryer, kiln, greenhouse, or other thermal application. In these projects, the gas is piped directly to a nearby customer for use in combustion equipment as a replacement or supplementary fuel. Only limited condensate removal and filtration treatment are required, although some modifications of existing combustion equipment might be necessary.

Landfill gas can also be used directly to evaporate leachate. Leachate evaporation using landfill gas is an option for landfills where leachate disposal at a water resource recovery facility is unavailable or expensive. Landfill gas is used to evaporate leachate to a more concentrated and more easily discarded effluent volume.

Use for medium-Btu gas includes firing pottery and glass-blowing kilns; powering and heating greenhouses; and evaporating waste paint. Current industries using landfill gas include, for example: (i) the auto manufacturing industry, (ii) the chemicals production industry, (iii) the food and beverage processing industry, (iv) the pharmaceuticals industry, (v) the cement and brick manufacturing industry, (vi) the wastewater treatment industry, and (vii) the paper and steel production industries.

Landfill gas can be upgraded to renewable natural gas (RNG), a high-Btu gas, through treatment processes by increasing its methane content and, conversely, reducing the content of carbon dioxide, nitrogen, and oxygens. Renewable natural gas can be used in place of fossil natural gas, as pipeline-quality gas, compressed natural gas (CNG), or liquefied natural gas (LNG). Options for use of renewable natural gas include thermal applications, to generate electricity or as fuel for vehicles. The renewable natural gas can be used locally at the site where the gas is produced or can be injected into natural gas transmission or distribution pipelines for delivery to another location.

See also: Biogas, Gas Cleaning, Gas Processing, Gas Treating, Landfill Leachate, Landfill Leachate Management, Waste, Waste-To-Energy.

Landfilling

Provided that there is no shortage of land with suitable geological formations, landfill remains the principal final disposal route for the majority of wastes, even in highly industrialized countries. Over 70% of municipal wastes in North America and Western Europe are landfilled with little or no treatment. Where there is treatment, it is usually designed to reduce the volume of waste to be landfilled and includes compaction, shredding, baling, and incineration. Most solid wastes will directly be disposed of in sanitary landfills where there is some protection for citizens against airborne dust and litter, stench, rodents, and insects. Most of these nuisances can be prevented by the prompt covering of freshly dumped waste with soil.

In addition to landfill gas, the other product of landfill chemistry is landfill leachate. This is a liquid formed within a landfill site that is comprised of the liquids that enter the site (including rainwater) and the material that is leached from the wastes as the infiltrating liquids percolate downwards through the waste.

The main environmental problem associated with landfilling is pollution of groundwater. Rainwater percolating through solid waste tends to carry large amounts of pollutants to groundwater aquifers if the underlying strata are pervious or fissured. Thus, wells drawing from the aquifers will be extracting groundwater contaminated by the leachate; such a situation is often difficult to remedy. The leachate from solid wastes may have a pollution load up to 15 to 20 times higher than domestic wastewater.

Landfill tends to predominate as a waste disposal mode because it is regarded as an effective but low-cost method of disposal, also for hazardous waste. Even where other methods are more suitable for environmental reasons, the higher capital and (short-term) running costs mean that they cannot compete without government intervention. However, such cost calculations take no account of the longer term. In the long run, landfill of hazardous materials may impose a larger financial burden than other methods because of the high cost of ensuring that the site remains secure for the time it takes for the waste to be rendered harmless.

Disposal to landfill of untreated wastes other than inert material is becoming less acceptable, partly in response to a few well-documented instances where poorly-designed and operated landfills are giving rise to pollution problems, and partly as a result of greater public awareness of the issues involved.

See also: Landfill Leachate, Waste.

Landfill Leachate

Leachate is the liquid that drains or leaches from a landfill, and it varies widely in composition regarding the age of the landfill and the type of waste that is contained in the landfill. The leachate may also be a useful starting material for the production of fuels and chemicals and should not be rejected as such until it (the leachate) has been tested for that potential.

The principal organic content of leachate (that could be the basis for the production of alternative fuels) formed during the breakdown processes varies with the location and the types of materials sent to the landfill. However, the organic content can be measured in terms of (i) the biochemical oxygen demand, BOD, (ii) the chemical oxygen demand, COD, or (iii) the total organic carbon, TOC. Also, the quality of municipal landfill leachate changes with time as the degradation of the waste continues inside the landfill. The degradation process is generally divided into five successive stages, namely, (i) aerobic, (ii) hydrolysis and fermentation, (iii) acetogenesis, (iv) methanogenic, and (v) aerobic phase (Figure 7.2). These processes are dynamic as each stage being dependent on the creation of a suitable environment by the preceding stage.

The concentration of certain compounds like nitrogen, ammonium, phosphorus, and chloride do not (typically) change significantly between the decomposition phases. Ammonia is probably the most important inorganic contaminant with the greatest potential to adversely impact on surface water and groundwaters. However, other components (such as heavy metals and sulfide derivatives) may be significant in certain circumstances. Iron and calcium are particularly important with respect to the precipitation of solids, while elevated salinity levels are ubiquitous. It should be noted that the site-specific discharge requirements will determine the components that require treatment or removal.

The generation of the leachate is caused principally by rain or melted snow percolating through waste deposited in a landfill. Once in contact with decomposing solid waste, the percolating water becomes contaminated, and if it then

flows out of the waste material, it is termed leachate. Additional leachate volume is produced during this decomposition of carbonaceous material producing a wide range of other materials including methane, carbon dioxide, and a complex mixture of organic acids, aldehydes, alcohols, and simple sugars.

One of the most important problems with designing and maintaining a landfill is managing the leachate that is generated when water passes through the waste. The leachate consists of many different organic and inorganic compounds that may be either dissolved or suspended. Regardless of the nature of the compounds, they pose a potential pollution problem for local ground and surface waters.

The use of landfill liners is now mandatory within both the United States and the European Union except where the waste is deemed inert. In addition, most toxic and difficult materials are now specifically excluded from landfilling. However, despite much stricter statutory controls, leachates from modern sites are found to contain a range of contaminants that may either be associated with some level of illegal activity or may reflect the ubiquitous use of a range of difficult materials in household and domestic products which enter the waste stream legally.

The physical appearance of leachate when it emerges from a typical landfill site is a yellow- or orange-colored cloudy liquid with a strong odor. The smell is typically acidic and offensive and may be very pervasive because of hydrogen-, nitrogen-, and sulfur-rich organic species such as mercaptans [thiols, i.e., organic compounds containing the thiol (SH) function].

Many factors influence the production and composition of leachate. One major factor is the climate of the landfill. For example, where the climate is prone to higher levels of precipitation, there will be more water entering the landfill and therefore more leachate generated. Another factor is the site topography of the landfill that influences the runoff patterns and again the water balance within the site.

Current leachate treatment options include recycling and re-injection, on-site treatment, discharge to a municipal water treatment facility, or a combination. However, with stricter regulations regarding ground and surface water contamination, landfills have to find new treatment alternatives.

The vast majority of wastes will produce a leachate of sorts if water is allowed to percolate through it, but the proportions of the leachate constituents are chiefly determined by the composition and solubility of the waste components. For example, if the waste is changing in composition (for example due to weathering or biodegradation), then leachate quality will change with time. This is particularly the case in landfills containing municipal waste.

At the start, the leachate produced is typically generated under the aerobic, oxygen-rich conditions, and this produces a complex solution with near neutral pH of 7.5. This process generally only lasts a few days or weeks and is relatively unimportant in terms of the quality of the leachate. However, the heat produced during aerobic decomposition can sometimes rise to as high as 80 to 90°C (175 to 195°F), and if this heat is retained, it can enhance the later stages of leachate production.

As waste decomposition progresses, the oxygen within the waste gradually becomes diminished, and the conditions become anaerobic. This initially creates high concentrations of soluble degradable organic compounds and an acidic pH. Ammonium and metal concentrations also rise during this phase. After several months or years, the onset of methanogenic conditions changes the pH of the leachate, making it more neutral or even slightly alkaline. As biodegradation nears completion, aerobic conditions may return, and the leachate will eventually cease to be hazardous to the environment.

The character of the leachate can be determined by means of the toxicity characteristic leaching procedure (TCLP).

See also: Acetogenesis, Acidogenesis, Aerobic Digestion, Anerobic Digestion, Hydrolysis and Fermentation, Landfill Gas, Landfilling, Methanogenesis, Toxicity Characteristic Leaching Procedure.

Landfill Leachate Management

Leachate produced in a landfill is a liquid which has percolated through the waste, thereby leaching suspended and soluble materials that originate from or are products of the degradation of the waste. However, before considering the design of any leachate management system, it is important to consider the objectives that are to be achieved. Leachate needs to be controlled in a landfill for the following reasons: (i) to reduce the potential for seepage out of the landfill through the sides or the base either by exploiting weaknesses in the liner or by flow through its matrix, (ii) to prevent liquid levels rising to such an extent that rising liquid levels can spill over and cause pollution to

ditches, drains, and water courses or water systems, (iii) to influence the processes leading to the formation of landfill gas, chemical and biological stabilization of the landfill, (iv) to minimize the interaction between the leachate and the liner, and (v) in the case of above ground landfill, to ensure the stability of the waste.

Part of any leachate management plan should include definitive information that describes the manner in which the leachate is to be managed and measures put in place to minimize the generation of the leachate. Also, details on the leachate recirculation rate (if included in the plan) and a discussion of the means by which the leachate will be continually monitored as well as the performance and state of the liner which will relate to leachate recirculation, and the hydraulic loading of the landfills leachate collection and removal system should also be included. The plan should also address such items as the potential for leachate surface seeps, odor, remedial cleaning/flushing of the leachate collection, and removal system to ensure free-flow conditions and the potential for increased leachate leakage through the liner.

Landfill Mining

Landfill mining and reclamation (LFMR) is a process whereby solid wastes which have previously been landfilled are excavated and processed. The function of landfill mining is to reduce the amount of landfill mass encapsulated within the closed landfill and/or temporarily remove hazardous material to allow protective measures to be taken before the landfill mass is replaced.

In the process, mining recovers valuable recyclable materials, a combustible fraction that may serve as a precursor to fuel, soil, and landfill space. The aeration of the landfill soil is a secondary benefit as a consequence of regrading the landfills' future use. The overall appearance of the landfill mining procedure is a sequence of processing machines laid out in a functional conveyor system. The operating principle is to excavate, sieve, and sort the landfill material.

The concept of landfill mining was introduced when it was recognized that waste contains many resources with high value – the most notable of which are non-ferrous metals such as aluminum cans and metal scrap. The concentration of aluminum in many landfills is higher than the concentration of aluminum in bauxite from which the metal is derived. However, the potential to mine a fuel precursor such as wood or compressed organic material adds extra impetus to the concept of landfill mining.

Mining of landfill sites that were created for specific purposes is often the easiest form of landfill mining. However, mining municipal landfills has to be based on the expected content of the landfill.

Older landfills in the United States were often capped and closed, essentially entombing the waste. This can be beneficial for waste recovery. It can also create a higher risk for toxic waste and leachate exposure as the landfill has not fully processed the stewing wastes. Mining of bioreactor landfills and properly stabilized modern sanitary landfills provides its own benefits. The biodegradable wastes are more easily sieved out, leaving the non-biodegradable materials readily accessible. The quality of these materials for recycling and reprocessing purposes is not as high as initially recycled materials. However, materials such as aluminum and steel are usually excluded from this.

Landfill mining is most useful as a method to remediate hazardous landfills. Landfills that were established before landfill liner technology was well established often leak their unprocessed leachate into underlying aquifers. This is both an environmental hazard and also a legal liability. Mining the landfill simply to lay a safe liner is a last, but sometimes necessary resort.

In the mining process, an excavator or front end loader uncovers the landfilled materials and places them on a moving floor conveyor belt to be taken to the sorting machinery. A trommel (also known as a rotary screen) is a mechanical screening machine used to separate materials by size. First, a large trommel separates materials like appliances and fabrics. A smaller trommel then allows the biodegraded soil fraction to pass through leaving non-biodegradable, recyclable materials on the screen to be collected. An electromagnet is used to remove the ferrous material from the waste mass as it passes along the conveyor belt. A front end loader is used to move sorted materials to trucks for further processing. Odor control sprayers are wheeled tractors with a cab and movable spray arm mounted on a rotating platform. A large reservoir tank mounted behind the cab holds neutralizing agents, usually in liquid form, to reduce the smell of exposed wastes.

Excavators dig up waste mass and transport it, with the help of front end loaders, onto elevator and moving floor conveyor belts. The conveyor belts empty into a coarse, rotating trommel. The large holes in the screen

allow most wastes to pass through, leaving behind the over-sized, non-processable materials. The over-sized wastes are removed from inside the screen. The coarse trommel empties into the fine rotating trommel. The fine rotating trommel allows the soil fraction to pass through, leaving mid-sized, non-biodegradable, mostly recyclable materials. The materials are removed from the screen. These materials are put on a second conveyor belt where an electromagnet removes any metal debris. Depending on the level of resource, recovery material can be put through an air classifier which separates low-boiling organic material from high-boiling organic material. The separate streams are then loaded, by front end loaders, onto trucks either for further processing or for sale. Further manual processing can be done on site if processing facilities are too far away to justify the transportation costs.

Landfill mining is also possible in countries where land is not available for new landfill sites. In this instance, landfill space can be reclaimed by the extraction of biodegradable waste and other substances then refilled with wastes requiring disposal.

There are several proposals to use the mined landfill as feedstock to an anaerobic digester. However, there are some drawbacks to anaerobic digesters, mainly relating to the type of feedstock used. If the feedstock contains toxic chemicals (such as pesticides and wood preservatives), the digestate will be highly toxic through concentration of the toxic constituents. If the digestate cannot be used as a fertilizer, it becomes waste once more – but, having been mined from an old site, it will, more than likely, be classified as a toxic waste.

See also: Landfill Gas – Extraction, Landfill Waste – Gasification.

Landfill Sites

A landfill site is an area of land that has been specifically engineered to allow for the deposition of waste on to and into it. Municipal solid waste landfill sites are a large source of human-related methane emissions and, in some countries such as the United States, can account for up to 25% of these emissions. At the same time, methane emissions from landfills represent a lost opportunity to capture and use a significant energy resource.

The design of a landfill site should be such that it will prevent, or reduce as far as possible, negative effects on the environment, as well as the risks to human health arising from the landfilling of waste. It is essential that the design include methods, standards, and operational systems based on best practice which reflect progress in landfill management and containment standards. Landfill design is an interactive process incorporating (i) the conceptual design proposals, (ii) the findings of the environmental assessment and environmental monitoring results, (iii) risk assessment, and (iv) the fundamental objective behind waste management is that of sustainability.

The primary objective of landfill site design is to provide effective control measures to prevent or reduce as far as possible negative effects on the environment, in particular the pollution of surface water, groundwater, soil, and air, as well as the resulting risks to human health arising from landfilling of waste. The design concept for a landfill depends on the ground conditions, the geology and hydrogeology of the site, the potential environmental impacts, and the location of the landfill. The investigations for a landfill should provide sufficient information to enable the formulation of a site-specific design.

Landfill practice is dynamic in that it will change with both advances in technology and changes in legislation. To incorporate such advances and changes, a periodic review of the design should be carried out, as the lifespan of a landfill site from commencement to completion is long compared to other construction projects. Generally, landfills are constructed on a phased basis during which all environmental media that may be significantly impacted through the life of the landfill should be considered.

A liner must be provided for the protection of soil, groundwater, and surface water. The liner system may consist of a natural or artificially established mineral layer combined with a geosynthetic liner that must meet prescribed permeability and thickness requirements.

An efficient leachate collection system may have to be provided to ensure that leachate accumulation at the base of the landfill is kept to a minimum. The leachate system may consist of a leachate collection layer with a pipe network to convey the leachate to a storage or treatment facility.

The accumulation and migration of landfill gas must be controlled. Landfill gas may need to be collected with subsequent treatment and utilization, or disposal in a safe manner through flaring or venting.

Provisions should be incorporated in the design to minimize and control nuisances arising from the construction, operation, closure, and aftercare phases of the landfill. Nuisances that may arise from landfilling include noise, odors, dust, litter, birds, vermin, and fires.

Consideration must be given to the stability of the subgrade, the basal liner system, the waste mass, and the capping system. The subgrade and the basal liner should be sufficiently stable to prevent excessive settlement or slippages. The hydraulic uplift pressure on the lining system due to groundwater must be considered. The method of waste emplacement should ensure stability of the waste mass against sliding and rotational failure. The capping system should be designed to ensure stability against sliding. Visual appearance and landscape consideration should be given to the visual appearance of the landform during operation and at termination of landfilling and its impact on the surrounding landforms.

The designer must also consider the manner of site development and the necessary site infrastructural requirements during landfill operation and restoration. Landfill sites should be developed on a phased basis. Site infrastructure should include for the provision of (i) site accommodation, (ii) weighbridge, (iii) waste inspection area, (iv) wheel wash, (v) site services, and (vi) security fencing.

The designer should consider the intended after-use of the facility. It should be compatible with the material components and physical layout of the capping system, the surrounding landscape, and current land use zoning as specified in the relevant development plan.

Landfill Sites – Bioreactor

An innovative approach to municipal solid waste disposal, which actually encourages rapid waste decomposition and speed stabilization, is the bioreactor landfill. The enhanced waste degradation and stabilization, carried out by the indigenous microbial populations within the waste, is accomplished through control of moisture, temperature, pH, nutrients, etc. The enhanced microbiological processes within a bioreactor can transform and stabilize the decomposable organic waste within 5 to 10 years of implementation, compared with many decades for conventional landfills where wastes are essentially sealed off from air and moisture.

The bioreactor landfill was initially defined by the Solid Waste Association of North America (SWANA) as (quote) a sanitary landfill operated for the purpose of transforming and stabilizing readily and moderately decomposable organic waste constituents within 5 to 10 years following closure by purposeful control to enhance microbiological processes (end quote). The bioreactor landfill significantly increases the extent of waste decomposition, conversion rates, and process effectiveness over what would otherwise occur within the landfill. SWANA now defines a bioreactor landfill as (quote) any permitted Subtitle D landfill or landfill cell, subject to New Source Performance Standards/Emissions Guidelines (NSPS/EG), where liquid or air, in addition to leachate and landfill gas (landfill gas) condensate, is injected in a controlled fashion into the waste mass in order to accelerate or enhance biostabilization of the waste (end quote). However, there is still disagreement among scientists and engineers as to the precise definition for a bioreactor landfill.

A bioreactor landfill is typically a municipal solid waste landfill site that operates to rapidly transform and degrade organic waste. The increase in waste degradation and stabilization is accomplished through the addition of liquid and air to enhance microbial processes. There are three types of bioreactor landfills: (i) an aerobic landfill, (ii) an anaerobic landfill, and (iii) a hybrid landfill, which is a combination of the aerobic process and the anaerobic process.

In an aerobic bioreactor landfill, leachate is removed from the bottom layer, piped to liquids storage tanks, and re-circulated into the landfill in a controlled manner. Air is injected into the waste mass using vertical or horizontal wells to promote aerobic activity and accelerate waste stabilization. In an anaerobic bioreactor landfill, moisture is added to the waste mass in the form of re-circulated leachate and other sources to obtain optimal moisture levels. Biodegradation occurs in the absence of oxygen (anaerobically) and produces landfill gas. Landfill gas (primarily methane) can be captured to minimize greenhouse gas emissions and can be used for energy projects. Hybrid (Aerobic-Anaerobic) – The hybrid bioreactor landfill accelerates waste degradation by employing a sequential aerobic-anaerobic treatment to rapidly degrade organics in the upper sections of the landfill and collect gas from lower sections. Operation as a hybrid results in the earlier onset of methanogenesis compared to aerobic landfills. In all cases, leachate is formed when rain water filters through wastes placed in a landfill. When this liquid comes in

contact with buried wastes, it leaches, or draws out, chemicals or constituents from those wastes. Thus, in contrast to conventional municipal solid waste landfills, bioreactors are designed and operated to enhance microbial processes significantly, to degrade and stabilize the organic constituents of the waste.

In a bioreactor landfill, leachate and additional liquid are returned to the landfill until the liquid holding capacity of the waste is achieved. Leachate drained from the waste is recovered and recirculated to maintain the moisture content of the waste and distribute nutrients for microbial degradation. A distinction should be made between the bioreactor landfill operation and the conventional leachate recirculation performed at conventional municipal solid waste landfill sites. The bioreactor process requires significant liquid addition to maintain optimal conditions.

Leachate alone is usually insufficient to sustain the bioreactor needs. Water or non-toxic, non-hazardous liquids and semi-liquids are suitable amendments to supplement leachate. At the closure of a bioreactor landfill site, the following should be observed: (i) the leachate quantity will be amenable to on-site treatment with limited need for off-site transfer, treatment, and/or disposal, (ii) the generation of the landfill gas generation should be in decline, and (iii) the long-term environmental risk will be minimized.

Landfill Sites – Construction and Debris

A construction and debris landfill site (sometimes designated as an *inert landfill site*) is devoted exclusively to construction and debris wastes that are chemically and physically stable and do not undergo decomposition. Such wastes are sand, bricks, concrete, or gravel. The waste, as the name implies, is generated from construction, renovation, repair, and demolition structures such as residential and commercial buildings, roads, and bridges. The composition of construction and debris waste varies for these different activities and structures.

Overall, construction and debris waste is composed mainly of wood products, asphalt, drywall, and masonry; other components often present in significant quantities are metals, plastics, earth, shingles, insulation, paper, and cardboard. Construction and debris also contain wastes that may be hazardous, potentially toxic and problematic, such as adhesives, leftover paint, excess roofing cement, waste oils, grease and fluids, batteries, fluorescent bulbs, appliances, carpet, and treated or untreated wood. It is not prudent to dispose of such waste in municipal solid waste landfill sites. Construction and debris landfills are easier to site because demolition materials are for the most part inert unless contaminated from an external source introduced at the construction/demolition site; therefore, the environmental impact is considered minimal.

Landfill Sites – Hazardous Waste

A *hazardous waste landfill site* is a waste disposal site that is units constructed to specific design criteria and which receive wastes meeting the local definition of hazardous waste. These landfills are generally constructed to be secure repositories for material that presents a serious hazard to human health, such as high-level radioactive waste. They are restricted, by permit or law, to the types of waste that they may handle (chemical vs. radioactive, liquid vs. dry). Double liner systems are the norm for hazardous waste landfills.

Thus, these types of facilities are disposal facilities for the more toxic chemicals and dangerous by-products. These landfills must be extremely well engineered to reduce any chance of the escape of hazardous compounds into the environment. These landfills are restricted, by permit or law, to the types of waste that they may handle (chemical vs. radioactive, liquid vs. dry). Double liner systems are the norm for hazardous waste landfills.

See also: Hazardous Waste, Waste.

Landfill Sites – Manual

Manual landfills have been developed in South and Central American cities where population sizes are less than 50,000 inhabitants. Manual landfills are similar in design to mechanized ones except for the size and the equipment required. These landfills have the capacity to receive 10 to 50 tons per day. The use of heavy equipment may be

required but only for periodic preparation for the terrain and the accumulation of cover material. Otherwise, all key steps for landfill preparation are carried out manually including cell preparation, compaction, and daily cover.

In some cases, a manual landfill site may also be designated as a *dump site* which is a landfill site that is not engineered with the special protective measures required by a sanitary landfill. Dump sites are most common in rural, remote, and developing areas. Many jurisdictions prohibit the use of a non-sanitary landfill for the disposal of municipal solid waste. Other jurisdictions that do allow dumps may require them to be constructed according to some engineering standard to mitigate the risk of environmental contamination, such as by (i) limiting the angle of the slope, (ii) requiring compaction of the waste in place, or (iii) ensuring that the cell is sufficiently high enough above the groundwater table to mitigate the potential for contamination of the water.

Landfill Sites – Municipal Solid Waste

Conventional municipal solid waste landfill sites (MSWLF) generally contain (less toxic) wastes from sources such as private homes, institutions, schools, and businesses without hazardous wastes. Modern sanitary landfills are engineered to protect public health and the environment and usually include detection and prevention of hazardous waste from entering the landfill, appropriate cover material for active cells and closed landfill, disease vector and explosive gas control, air monitoring, facility access, run-on control, run off control and surface water requirements, restrictions on liquids entering the cells, and record-keeping requirements. An engineered municipal solid waste landfill site comprises a liner, leachate collection and removal system, final cover, gas management, and a groundwater monitoring system.

Landfill Sites – Sanitary

A *sanitary landfill site*, also called a modern, engineered, or secure landfill site, typically has physical barriers such as liners and leachate collection systems, and procedures to protect the public from exposure to the disposed wastes. The term sanitary landfill normally refers to those sites where municipal solid waste is sent for disposal as well as other wastes that are high in organic material. In some countries, all landfills are sanitary landfills.

Landfill Sites – Surface Impoundment

A surface impoundment is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials (although it may be lined with man-made materials), which is designed to hold an accumulation of liquid wastes or wastes containing free liquids. Examples of surface impoundments are holding, storage, settling, and elevation pits, ponds, and lagoons. If the pit, pond, or lagoon is intended for storage or holding without discharge, it is considered to be a surface impoundment. This information can be used for direct calculation of the quantity of a listed chemical and/or compound disposed of in this manner. This disposal method is often considered as a release to land; however, chemicals in the impoundment may be released to air by volatilization, collected as sludge and removed, or biodegraded. Any releases from the impoundment should be accounted for in release totals to air, water, land, or offsite disposal.

The impoundments must be properly lined to prevent infiltration of chemical constituents into the soil and protect groundwater quality. The liner is considered as part of the impoundment, and waste migration into the liner is allowed. The liner must therefore have sufficient strength and thickness to prevent failure due to pressure gradients, be chemically compatible with the migrating waste constituents, be protected from climatic conditions, installation and operation stresses, and prevents gradients caused due to settlements, compression or uplift.

A surface impoundment unit used for disposal of hazardous waste must have two or more liners and a leachate collection and removal system between such liners. The liner system must include a top liner made of geomembrane. The requirements for a hazardous waste landfill are similar to those for a surface impoundment. The system must have a leachate collection system, a top flexible membrane liner (FML), a leachate collection, and a detection and removal system.

A sustainable flood retention basin (SFRB) is defined as an impoundment or wetland that has the potential or predefined role for use in flood defense and pollution control, which is accomplished cost-effectively through best

management practice achieving flood risk management while enhancing sustainable drainage, pollution reduction, biodiversity, green space, and recreational opportunities for society (Yang *et al.*, 2011). The sustainable flood retention basin must be capable of being maintained at a steady level without exhausting natural resources, harming the environment, and causing severe ecological damage. The functions of retention basins are therefore diverse. Moreover, one basin often has multiple and mixed functions and the classification of a sustainable flood retention basin is required to allow for better understanding and communication of the status and function of any basin.

Whatever the classification, the landfill site should be designed in such a fashion that there is minimal harm to the environment and that the land may be restored in some way after the period of waste disposal. Despite its connotations as an *out of sight, out of mind* solution (Hester and Harrison, 2002, page 28), landfill is a well-used method of waste management that is applied to the majority of solid wastes in many countries.

See also: Waste.

Landfill Waste – Gasification

There is also the potential for the gasification of any organic waste material that is mined from the landfill as a solid or semi-solid.

A waste gasification facility converts the waste into a pressurized gas mixture which is then passed through a cleanup system to remove particulate matter and tar vapor, and finally used to turn turbines in a power plant. The remaining gas is a mixture of carbon monoxide, hydrogen, water vapor, and carbon dioxide. Finally, the particulates and tar are thermally treated (pyrolyzed) to produce carbon monoxide.

Any hydrogen produced that is not used as a constituent of synthesis gas can be removed and stored for use in hydrogen fuel cells. Waste gasification does produce some carbon dioxide that needs attention. There is the thought that although the carbon dioxide is produced from a renewable organic source, it has a short atmospheric residence time and therefore does not contribute to global warming. On this basis, carbon dioxide from biomass is acceptable but carbon dioxide from a fossil fuel is unacceptable.

The goal of using fuels from alternative sources is not only to supplement the dwindling supplies of fossil fuels but also to reduce the emissions of greenhouse gases. Carbon dioxide is a greenhouse gas – no matter what the source. To consider the carbon dioxide allowable because it is from a biomass-based process is, in any sense, playing with numbers and using a statistical means to justify the end.

See also: Gasification, Gasification of Biomass, Synthesis Gas.

Landfill Waste – Power Generation

Large municipal or industrial landfills produce gas that can be tapped to generate electricity. Microorganisms that live in organic materials such as food wastes, paper, or yard clippings cause these materials to decompose. This produces landfill gas, typically comprised of roughly 60% methane and 40% carbon dioxide.

The gas generated in landfills can be tapped after the completion of the landfill, and when burnt as fuel, has a calorific value approximately half that of natural gas. This is due to the fact that there is only approximately 60% combustible methane in the gas created and this has a calorific value of approximately 450 Btu/ft³ compared to approximately 900 Btu/ft³ for purified natural gas.

Generating electricity from landfill gas is clearly a better sustainable solution than merely trapping and not using it in any productive manner. It is a resource that should be employed. There is the added bonus for the site operators of extra generated financial revenue from the electricity sales. However, all of the environmental burdens still apply, but there is the offset that electricity generation by non-renewable sources can be reduced.

Landfill gas is collected from landfills by drilling wells into the landfills, and collecting the gases through pipes. Once the landfill gas is processed, it can be combined with natural gas to fuel conventional combustion turbines or used to fuel small combustion or combined cycle turbines. Landfill gas may also be used in fuel cell technologies, which use chemical reactions to create electricity, and are much more efficient than combustion turbines. However, use of the gas produced by landfills may reduce the harmful environmental impacts that would otherwise result from

landfill operations. Landfill gas electricity generation offers major air quality benefits where landfills already exist or where the decision to build the landfill has already been made.

A landfill gas power plant burns methane that would otherwise be released into the atmosphere or burned off in a flaring process. Landfill gas combustion produces some carbon dioxide, but the impact of these emissions on global climate change is offset many times over by the methane emission reductions.

Landfill gas generators produce nitrogen oxides emissions that vary widely from one site to another, depending on the type of generator and the extent to which steps have been taken to minimize such emissions. Combustion of landfill gas can also result in the release of organic compounds and trace amounts of toxic materials, including mercury and dioxins, although such releases are at levels lower than the releases when the landfill gas is flared.

Unlike other power plants that rely upon water for cooling, landfill gas power plants are small, and therefore pollution discharges into local lakes or streams are typically quite small.

See also: Landfill Gas – Composition, Landfill Gas – Extraction.

Leaching

Leaching is a natural process by which water-soluble substances (such as water-soluble chemicals or hydrophilic chemicals) are washed out from soil or waste disposal areas (such as a landfill). These leached out chemicals (leachates) can cause pollution of surface waters (ponds, lakes, rivers, and the sea) and sub-surface water groundwater aquifers).

The solvent used for leaching processes can be a subcritical liquid or a supercritical fluid. It must compete with forces binding the solute to the solid in order to solubilize it. These forces can be very weak, as with oil contamination on mill scale, of intermediate strength, as with adsorbed contaminants on clay or activated carbon, or strong, as with chemical binding of metals in ores. Correspondingly, the solvents used to dissolve the solute can vary from those having purely physical interactions through those having weak chemical interactions (such as polar forces), through those having intermediate strength chemical forces (such as chemical complexing), to those exhibiting the strong chemical forces of ionic bonding. Once the solute has been solubilized in the solvent by the leaching process, it can be treated further by other processes, including liquid-liquid extraction, to purify and recover the solute, i.e., the leachate.

The basic difference between leaching and the other extraction processes is that a *solid* rather than a fluid must be intimately mixed with and then separated from the solvent. This may require longer residence times for the solvent-solid mixture to come to equilibrium in each contacting stage. This is especially true if the solid is porous, and the solvent must diffuse into the pores to dissolve the desired solute. The solvent needs to fulfill two major functions to be a good leaching solvent.

First, the solvent must be able to desorb the desired solute from the surface of the solid, and, second, it should be able to dissolve the released solute to keep it from being mechanically remixed with the feed solids and trapped in the matrix during phase separation. Thus, choosing a suitable solvent for a leaching operation requires some knowledge of the nature of the binding forces between the feed solids and the components to be recovered from them. For example, clay minerals tend to adsorb polar molecules more strongly than non-polar molecules. Thus, while clay minerals are effective for adsorbing polar components from non-polar solutions such as hydrocarbons, they are not effective for recovering organics from aqueous solutions because the strongly polar water molecules occupy the adsorption sites and cannot be displaced by the less polar organic molecules. However, to recover organics from spent clay, a small amount of water added to a good solvent for the organics will displace the organics from the surface of the clay very effectively. This permits the organic constituents to dissolve in the solvent and be recovered from the solids.

In contrast to the clay minerals, the carbon adsorbents tend to adsorb non-polar molecules more strongly than polar ones. This permits carbon to be used effectively to adsorb organics from aqueous wastewater solutions. However, to regenerate the spent carbon adsorbent requires a solvent of low solubility parameter to compete effectively for the weakly interactive adsorption sites on the carbon. The solvent can then dissolve the relatively non-polar solute released from the adsorbent. This, along with ease of solvent recovery from solids, is what made supercritical fluids look like attractive solvents for regenerating spent carbon from adsorption processes.

In the environment, leaching is the process by which chemicals or radionuclides are released from the solid phase into the water phase under the influence of mineral dissolution, desorption, and complexation processes as affected by pH, redox chemistry, and biological activity. The process itself is universal, as any material exposed to contact with water will leach components from its surface or its interior depending on the porosity of the material. In terms of the effect of pH (acidity or alkalinity), the leachability of a chemical; (i.e., the ability of the chemical to be leached from the source) can be enhanced by the occurrence of acid rain which can enhance the solubility of the chemical in the acidified water.

Thus, leaching is the process by which (in the current context) contaminants are released from the solid phase into the water phase under the influence of dissolution, desorption, or complexation processes as affected by acidity or alkalinity (the pH value). The process itself is universal, as any material exposed to contact with water will leach components from its surface or its interior depending on the porosity of the material under consideration. Leaching often occurs naturally with soil contaminants such as chemicals, with the result that the chemicals end up in potable waters.

Many chemicals occur in a mixture of different components in a solid (such as the metallic deposits on petroleum coke or metals in spent catalysts). In order to separate the desired solute constituent or remove an undesirable solute component from the solid phase, the solid is brought into contact with a liquid during which time the solid and liquid are in contact and the solute or solutes can diffuse from the solid into the solvent, resulting in separation of the components originally in the solid (leaching, liquid-solid leaching). In addition, leaching may also be referred to as extraction because the chemical is being extracted from the solid or the process may also be referred to as washing because a chemical is removed from a solid with water.

Leaching is affected by (i) the texture of the solid that holds the chemical to be leached, (ii) structure of the chemical to be leached, and (iii) water content of the solid which holds the chemical. If the solid holding the chemical is soil, then in terms of soil texture, for example, the proportions of sand, silt, and clay affect the movement of water through the soil. Coarse-textured soil contains more sand particles which have large pores, and the soil is highly permeable which allows the water to move rapidly through the pore system. On the other hand, chemicals (such as phosphate pesticides) carried by water through coarse-textured soil are more likely to reach and contaminate groundwater. On the other hand, clay-textured soils have low permeability and tend to retain more water and adsorb more chemicals from the water. This slows the downward movement of chemicals, helps increase the chance of degradation and adsorption to soil particles, and reduces the chance of groundwater contamination.

In terms of soil structure, loosely packed soil particles allow speedy movement of water through the soil while tightly compacted soil holds water back and does not allow the water to move freely through it. Plant roots penetrate soil, creating excellent water channels when they die and rot away. These openings and channels may permit relatively rapid water movement even through soil that contains clay minerals. On the other hand, the amount of water already in the soil has a direct bearing on whether rain or irrigation results in the recharging of groundwater and possible leaching of chemicals into an aquifer. Soluble chemicals are more likely to reach groundwater when the water content of the soil approaches or is at saturation. Saturation is typical in the spring when rain and snowmelt occur, but when soil is dry, the added water just fills the pores in the soil near the soil surface, making it unlikely that the water will reach the groundwater supply.

Leaching processes introduce chemicals into the water phase by solubility and entrainment. In addition, the leaching processes that move chemicals from soil can have a variety of potential scenarios – the spill of chemicals on to soil may cause partitioning in water that has been in contact with the contamination.

See also: Pollutant Adsorption, Pollutant Solubility, Water.

Lean Gas and Rich Gas

Lean gas is a gas stream (especially a natural gas stream) in which methane is the major constituent and is the residual gas from the absorber after the condensable constituents have been removed from the wet gas. On the other hand, rich gas is a gas stream that contains higher-molecular-weight (and higher-boiling) hydrocarbon derivatives than a lean gas. Its liquid content adds important economic value to developments containing this type of fluid.

In terms, liquefied natural gas (LNG) that is of a specification with extremely low, high heating value (HHV). Lean liquid stream is predominately methane with some minor quantities of ethane and lean liquefied natural gas may be required to meet fuel quality specifications and standards required by liquefied natural gas-powered vehicles and other liquefied natural gas-fueled equipment. Leaner liquefied natural gas can be produced through the extraction of the heaviest components, namely the liquefied natural gas, propane, and butane. Rich liquefied natural gas with high heating value is also produced for some market segments.

On the other hand, rich liquefied natural gas is a gas stream that has a heat content that is higher than the standard on many North American pipelines, since it contains small amounts of natural gas liquids (NGLs). The natural gas liquids – typically ethane, propane, and butane – can be extracted following regasification and used as petrochemical feedstocks.

See also: Gas Cleaning, Natural Gas.

Life Cycle Impacts

The energy used to manufacture fertilizer and the fuel used to operate farm equipment at farms that grow biomass energy crops reduce the net energy produced from biomass power plants that use biomass crop systems for feedstock.

Life-cycle analyses of biomass have been conducted for various configurations of power plants and fuel supplies to determine the net energy available using biomass fuels for power generation. The results indicate that only 2% to 8% of the useful energy output of a biomass power plant fueled by a biomass crop system is required for fertilization, planting, cultivation, harvesting, transportation, and fuel preparation. In other words, the amount of useful energy output from a biomass power plant is 12.5 to 50 times as much as the energy required to grow, harvest, transport, and process biomass from biomass crop systems. While these studies have not addressed the implications of using forest-derived fuels instead of energy crops.

The transportation energy use for forest biomass may or may not be higher than for biomass crops. Transportation vehicles are similar, and so transportation distance would be the primary reason for differences in transportation energy use between biomass crops and forest biomass.

The net environmental benefits of ethanol depend on how much energy is used to grow and process the biomass feedstock. The ethanol fuel industry has made great efficiency gains. The current energy balance for ethanol is 1.34; that is, for every unit of energy used in growing and producing ethanol, approximately one-third more energy is produced as fuel. Current trends predict that this ratio will increase to 2.09 for corn ethanol and 2.62 for cellulose ethanol.

Ethanol made from corn will result in a net air emissions reduction of 20%. Using soybeans will reduce net emissions nearly 80%. Cellulose-based ethanol can lead to even greater decreases since this type of biomass can be used to generate more electricity than is used in the production of ethanol fuel. The surplus power can then be sold, displacing the burning of fossil fuels for electricity production. This can result in a net reduction greater than 100%. In the case of ethanol from corn stover, the reduction can be as much as 113%. Another study used total fuel cycle analysis to compare reformulated gasoline (RFG) to E10 (a mixture of 10% ethanol with 90% unleaded gasoline by volume) and E95 (a mixture of 95% ethanol with 5% unleaded gasoline). 91 E95 produces only 9% of the net CO₂ produced by the RFG fuel cycle. If one takes into account the carbon sequestration benefits, E95 produces only 4% of the total CO₂ produced by the RFG cycle.

Light Ends

The term light ends is a general collective term that is used to describe the gaseous and more volatile liquid hydrocarbon derivatives produced in a refinery or, in the present context, during the thermal treatment of biomass to produce gases and bio-oil. The term is equally applicable to a mixture of low-boiling products (i.e., gases) produced from alternate energy sources. The term usually includes the C₁ to C₄ hydrocarbon derivatives but may also include the C₅ and C₆ hydrocarbon derivatives (Table L-3).

Table L-3 Examples of the hydrocarbon constituents of light ends*.

Constituent	Formula	Boiling point	
		°C	°F
Alkanes			
Methane	CH ₄	-182	-296
Ethane	CH ₃ CH ₃	- 89	-128
Propane	CH ₃ CH ₂ CH ₃	-42	-44
n-Butane	CH ₃ CH ₂ CH ₂ CH ₃	-1	31
n-Pentane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	36	97
n-Hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	69	156
Alkenes*			
Ethylene	CH ₂ =CH ₂	-104	-155
Propylene	CH ₃ CH=CH ₂	-48	-54
Butylene-1	CH ₃ CH ₂ CH=CH ₂	-6	21
Butylene-2	CH ₃ CH=CHCH ₃	1	34

*Typically produced in thermal decomposition processes.

Light ends are produced in relatively small quantities during some processes (depending upon the temperature and the residence time of the feedstock in the hot zone). When a naphtha component at the time of its manufacture is passed through a condenser, most of the light ends do not condense and are withdrawn and handled as a gas. A considerable part of the light ends, however, can remain dissolved in the condensate, thus forming a liquid with a high vapor pressure.

A light ends unit consists of a sequence of distillation processes to separate the overhead distillate product from the atmospheric distillation column into five streams consisting of (i) methane, (ii) ethane, (iii) propane, (iv), butane (v), low-boiling naphtha, and (vi) high-boiling naphtha. The fractions consisting of methane, ethane, propane, and butane are often used as feedstock for chemicals production. Propane and butane are sold as liquefied petroleum gas (LPG). The low-boiling naphtha fraction that consists of the low-boiling paraffin hydrocarbons pentane (C₅H₁₂) and hexane (C₆H₁₄) is used as a blend-stock for gasoline production as may the high-boiling naphtha fraction, but if the high-boiling naphtha fraction is rich in cycloalkane derivative (also known as naphthene derivatives), it may be sent to a catalytic reforming unit to produce blend-stock for high-octane gasoline.

Gases and low-boiling liquids (such as light ends) with high vapor pressures may be stored in refrigerated tanks or in tanks capable of withstanding the pressures developed by the gases dissolved in the liquid. The more usual procedure, however, is to separate the light ends from the liquid by a distillation process generally known as *stabilization*. Enough of the light ends are removed to make a stabilized liquid, that is, a liquid with a low enough vapor pressure to permit its storage in ordinary tanks without loss of vapor.

Liquids with high vapor pressures may be stored in refrigerated tanks or in tanks capable of withstanding the pressures developed by the gases dissolved in the liquid. The more usual procedure, however, is to separate the light ends from the liquid by a distillation process generally known as *stabilization*. Enough of the light ends are removed to make a stabilized liquid, that is, a liquid with a low enough vapor pressure to permit its storage in ordinary tanks without loss of vapor. The simplest stabilization process is a stripping process. Low-boiling naphtha from a crude tower, for example, may be pumped into the top of a tall, small-diameter fractional distillation tower operated under a pressure of 50-80 psi. Heat is introduced at the bottom of the tower by a steam reboiler. As the naphtha cascades down the tower, the light ends separate and pass up the tower to leave as an overhead

product. Since reflux is not used, considerable amounts of liquid hydrocarbon derivatives pass overhead with the light ends.

Although the constituents of the light ends fraction do occur naturally as natural, gas and crude oil gases, they are also produced (in the case of crude oil) as a result of thermal (catalytic and non-catalytic) processes.

See also: Light Ends, Refining.

Light Hydrocarbons

Light hydrocarbon derivatives (low-boiling hydrocarbon derivatives) are those hydrocarbon derivatives with a molecular weight less than that of heptane (C_7H_{16} , molecular weight = 100). Typical hydrocarbons of the light ends group are the gases: methane, ethane, propane, and butane isomers, although on occasion, the pentane (C_5) isomers and the hexane (C_6) isomers may also be included in the light ends group.

See also: Light Ends, Refining.

Lightning

Lightning is a form of energy that occurs as an electrostatic discharge during which two electrically charged regions in the atmosphere or ground temporarily equalize themselves, causing the instantaneous release energy. This discharge may produce a wide range of electromagnetic radiation, from hot plasma created by the rapid movement of electrons to visible light. The three main kinds of lightning are distinguished by where they occur and are (i) inside a single thundercloud, (ii) between two different clouds, or (iii) between a cloud and the ground.

As a thundercloud moves over the surface of the Earth, an equal electric charge (of opposite polarity) is induced on the surface of the Earth (an image charge) underneath the cloud. The induced positive surface charge, when measured against a fixed point, will be small as the thundercloud approaches, increasing as the center of the storm arrives and dropping as the thundercloud passes. The referential value of the induced surface charge could be roughly represented as a bell curve. The oppositely charged regions create an electric field within the air between them, and this electric field varies in relation to the strength of the surface charge on the base of the thundercloud – the greater the accumulated charge, the higher the electrical field.

Since the late 1980s, there have been several attempts to investigate the possibility of harvesting energy from lightning. While a single bolt of lightning carries a relatively large amount of energy (approximately 5 billion joules), this energy is concentrated in a small location and is passed during an extremely short period of time (milliseconds); therefore, extremely high electrical power is involved. It has been proposed that the energy contained in lightning be used to generate hydrogen from water, or to harness the energy from rapid heating of water due to lightning, or to use inductors spaced far enough away so that a safe fraction of the energy might be captured.

A technology capable of harvesting lightning energy would need to be able to rapidly capture the high power involved in a lightning bolt. Several schemes have been proposed, but the ever-changing energy involved in each lightning bolt have rendered lightning power harvesting from ground based rods impractical. Additionally, lightning is sporadic, and therefore energy would have to be collected and stored; it is difficult to convert high-voltage electrical power to the lower-voltage power that can be stored. Another major challenge when attempting to harvest energy from lightning is the impossibility of predicting when and where thunderstorms will occur. Even during a storm, it is difficult to tell where exactly lightning will strike.

See also: Plasma.

Lignans

Lignans are traditionally defined as a class of secondary metabolites that are derived from the oxidative dimerization of two or more phenylpropanoid units. Despite the common biosynthetic origins, lignans exhibit a vast diversity in structure which leads to a well-established range of biological activities. Owing to these factors, lignans have proven to be a challenging and desirable synthetic target that has instigated the development of a number of different synthetic methods, advancing our collective knowledge toward the synthesis of complex and unique structures.

More generally, lignans are phenolic dimers possessing a 2,3-dibenzyl butane structure. Such compounds are known to exist as minor constituents of many plants, where they form the building blocks for the formation of lignin in the plant cell wall.

Structurally, lignans consist of two phenylpropane units linked together with β,β -bonds (Figure L-1). In some plants from the Magnoliales and Piperaceae family, some lignans have been identified that are linked together with other carbon-carbon bonds, which are referred to as neo-lignans (neolignans).

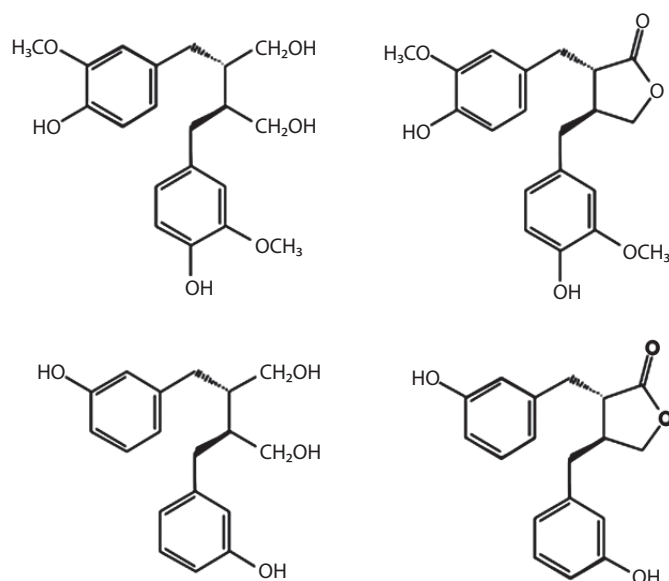


Figure L-1 Chemical structures of lignans.

Flaxseed contains by far the highest level of lignans, but vegetables, cereal brans, and legumes are also good sources, based on the amounts consumed in a high-fiber diet. Tea is also a good source of lignans.

See also: Flax and Flaxseed Oil, Lignin.

Lignin

Lignin is a complex biopolymer composed of different amounts of three monolignols, namely *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These propyl-phenol derivatives, which can be differentiated by their number of methoxy groups, include polar, hydroxyl, and carboxyl groups, which lead to the hydrophilic behavior in lignin. Lignin is a structural constituent of wood and (to a lesser extent) other plant tissues, which encrusts the walls and cements the cells together (Table L-4).

Table L-4 Amount (% w/w) of lignin common in various sources*.

Source	Lignin, % w/w
Bamboo	24-26
Cattle manure	2.7-5.7
Corn cobs	15
Corn stover	16-21
Grasses	10-30
Hardwood stem	18-25
Leaves	0
Newspaper	18-30
Nut shells	30-40
Paper	0-15
Rice straw	5.5
Softwood stem	25-35
Sugar cane bagasse	23-32
Sweet sorghum	11
Switchgrass	5-20
Waste papers from chemical pulps	5-10
Wheat straw	15-20

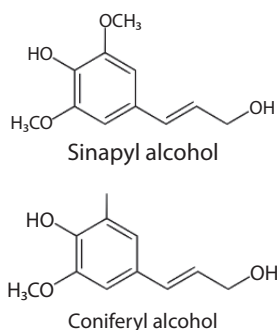
* The sources are listed alphabetically rather than in any other order.

See also: Table C-1.

An approximate classification of lignin derivatives is (i) softwood lignin, (ii) hardwood lignin, and (iii) grass lignin. There are several methods that can be used to separate the lignin, and therefore, various forms of lignin are available, such as milled wood lignin, dioxane lignin or enzymically liberated lignin, Kraft process lignin, and alkali lignin. Although the native lignin derivatives behave as an insoluble and three-dimensional chemical network, the isolated lignin derivatives often exhibit maximum solubility in solvents including dioxane, acetone, methyl cello-solve, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide.

The composition of lignin varies from species to species – as an example of composition from an aspen sample is carbon 63.4% w/w, hydrogen 5.9%, and oxygen 30% (by difference), mineral as 0.7% ash which corresponds to the approximate formula $(C_{31}H_{34}O_{11})_n$. As a biopolymer, lignin is unusual because of the heterogeneity and lack of a defined primary structure. Its most commonly noted function is the support through strengthening of wood. Structurally, lignin is a cross-linked polymer with a molecular mass in excess of 10,000, but the precise structure of lignin is unknown but it is believed to be a macromolecule, which consists of alkyl phenols and has a complex three-dimensional structure. Lignin is covalently linked with xylan derivatives in the case of hardwoods and with galactose-glucose-mannose units in softwoods. Lignin, together with hemicelluloses, acts as a cementing agent matrix of cellulose fibers in the woody structures of plants.

Lignin confers the hydrophobic properties reflecting the fact that it is based on aromatic ring systems. These three components are interwoven, and direct covalent linkages exist between the lignin and the hemicellulose. In chemical terms, the difference between hardwood and softwood is reflected in the composition of the constituent lignin. Chemically, hardwood lignin is primarily derived from sinapyl alcohol and coniferyl alcohol while softwood lignin is mainly derived from coniferyl alcohol.



Lignin is relatively hydrophobic and rich in aromatic subunits. The actual degree of polymerization is difficult to measure since the material is heterogeneous. The lignol derivatives that crosslink are of three main types, all derived from phenylpropane: 4-hydroxy-3-methoxy phenylpropane, 3,5-dimethoxy-4-hydroxy phenylpropane, and 4-hydroxy phenylpropane. The former tends to be more prevalent in conifers and the latter in hardwoods.

Different types of lignin have been described depending on the means of isolation. The three common monolignols presented below are (i) *trans*-coniferyl alcohol, (ii) *trans*-sinapyl alcohol, and (iii) *trans*-p-coumaryl alcohol. Thus, lignin can be defined as a polyphenolic material arising primarily from enzymic dehydrogenative polymerization of three phenylpropanoid units (p-hydroxy-cinnamyl alcohols). The proportions of the precursors in lignins vary with their botanical origin. Normal structural elements of softwood lignins are derived principally from *trans*-coniferyl alcohol (90%) with the remainder consisting mainly of *trans*-p-coumaryl alcohol. In contrast, hardwood lignins are mainly composed of *trans*-coniferyl alcohol and *trans*-sinapyl alcohol in varying ratios (about 50% for each alcohol).

Structural issues aside, lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components (structural acidic heteropolysaccharide derivatives contained in the primary cell walls of terrestrial plants), especially in vascular and support tissues. It is covalently linked to hemicellulose and therefore cross-links different plant polysaccharides, conferring mechanical strength to the cell wall and, by inference, to the whole plant.

Lignin plays a crucial part in conducting water in plant stems – the polysaccharide constituents of the plant cell are hydrophilic and thus permeable to water, whereas lignin is more hydrophobic and less permeable to water. The cross-linking of polysaccharides by lignin is an obstacle for water absorption to the cell wall and, thus, the presence of lignin makes it possible for the vascular tissue of the plant to conduct water efficiently.

Most lignin applications are based on technical lignins which are separated during pulping processes, and hydrolysis of lignin, which is obtained during wood acidic hydrolysis. The basic chemical phenylpropane units of lignin are bonded together by a set of linkages to form a complex matrix. This matrix comprises a variety of functional groups (such as hydroxyl, methoxyl, and carbonyl groups) which impart a high polarity to the lignin macromolecule.

The amount of extractable constituents is an important parameter which directly affects the heating value of wood (or, for that matter, any biomass). A high content of extractable constituents makes it desirable as fuel. The extractable constituents usually have low molecular weight and are soluble in neutral solvents. For example, terpene derivatives, lignan derivatives and other aromatic derivatives, fats, waxes, fatty acid derivatives and alcohol derivatives, turpentine, tannins, and flavonoids are categorized as extractable constituents. The contents of the extractable components vary among wood species, geographical site, and season and usually represent from between 3 to 10% by the weight of wood.

Lignin is a random polymer made up of phenyl propane units, where the phenol unit may be either a guaiacyl or syringyl unit. These units are bonded together in many ways, the most common of which are α -ether linkages or β -ether linkages. A variety of carbon-carbon linkages are also present, but are less common. The distribution of linkage in lignin is random because lignin formation is a free radical reaction that is not under enzymatic control. Lignin is highly resistant to chemical, enzymatic, or microbial hydrolysis due to extensive cross linking. Therefore, lignin is frequently removed simply to gain access to cellulose.

Lignin monomer units are similar to gasoline which has a high octane number, thus breaking the lignin molecules into monomers and removing the oxygen makes them useful as liquid fuels. The process for lignin conversion is mild hydrotreating to produce a mixture of phenolic and hydrocarbon materials, followed by reaction with methanol to produce methyl aryl ether.

The first step usually consists of two parts: hydrodeoxygenation (removal of oxygen and oxygen-containing groups from the phenol ring) and dealkylation (removal of ethyl or large side chains from the rings).

The major role is to carry out these reactions to remove the unwanted chains without carrying the reaction too far, which would lead to excessive consumption of hydrogen and produce saturated hydrocarbon derivatives, which are not as good octane enhancers as the aromatic compounds. Catalysts to carry out these reactions have dual functions. Metals such as molybdenum and molybdenum/nickel catalyze the deoxygenation, while the acidic alumina support promotes the carbon-carbon bond cleavage.

Although lignin chemicals have many applications such as in drilling mud, as binders for animal feed, and as the base for artificial vanilla, they have not been previously used as surfactants for oil recovery. Lignin chemicals can be used in two ways in chemical floods for enhanced oil recovery. In one method, lignosulfonates are blended with tallow amines and conventional petroleum sulfonates to form a unique mixture that costs approximately 40% less to use than chemicals made solely from petroleum or petroleum-based products. In the second method, lignin is reacted with hydrogen or carbon monoxide to form a new class of chemicals called lignin phenols. These phenols, because they are soluble in organic solvents, but not in water, are good candidates for further conversion to chemicals useful in enhanced oil recovery.

See also: Biomass, Cellulose, Coniferyl Alcohol, Hemicellulose, Lignans, Lignocellulose, Sinapyl Alcohol, Paracoumaryl Alcohol, Sinapyl Alcohol, Wood.

Lignocellulose

Lignocellulose (sometimes referred to as lignocellulosic biomass) has become a likely feedstock for the fuel and chemical industries in the event of an increase in oil and gas prices. Hemicellulose is a heteropolysaccharide built from different monosaccharides like pentoses and hexoses where xylose is predominant.

The features of lignocellulose that hinder enzyme access to the cellulose and hemicellulose include lignin content, hemicellulose content, acetyl content, cellulose crystallinity, degree of polymerization, and surface area and pore volume. Pretreatment of lignocellulose recalcitrance improves enzyme access by removing or altering lignin, removing hemicellulose, decrystallizing cellulose, and reducing the degree of polymerization in cellulose. The desirable characteristics of lignocellulose pretreatment process include preserving the cellulose and hemicellulose fractions, requiring minimal energy, and being effective on multiple lignocellulose feedstocks.

Lignocellulose is a complex matrix combining cellulose, hemicellulose, and lignin, along with a variable level of extractives. Cellulose is comprised of glucose, a six-carbon sugar, while hemicellulose contains both five- and six-carbon sugars, including glucose, galactose, mannose, arabinose, and xylose. The presence of cellulose and hemicellulose therefore makes lignocellulose a potential candidate for bioconversion. The ability of the bioconversion platform to isolate these components was initially limited, as the wood matrix is naturally resistant to decomposition.

By forming intramolecular and intermolecular hydrogen bonds between hydroxyl groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to be arranged parallel and form a crystalline macromolecular structure. Bundles of linear cellulose chains (in the longitudinal direction) form a microfibril which is oriented in the cell wall structure. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis.

The ramified structure makes hemicellulose more resistant than cellulose to hydrolyzation – it is chemically bound to lignin, and it binds lignin and cellulose.

See also: Cellulose, Hemicellulose, Lignin.

Limnology

Limnology is the study of fresh or saline waters contained within continental boundaries. Limnology and the closely related science of oceanography together cover all aquatic ecosystems. Limnology covers lakes, ponds, reservoirs, streams, rivers, wetlands, and estuaries, while oceanography covers the open sea. Limnology evolved into a distinct science only in the past two centuries, when improvements in microscopes, the invention of the silk plankton net,

and improvements in the thermometer combined to show that lakes are complex ecological systems with distinct structures. Today, limnology plays a major role in water use and distribution as well as in wildlife habitat protection. Limnologists work on lake and reservoir management, water pollution control, and stream and river protection, artificial wetland construction, and fish and wildlife enhancement.

Limnology is closely related to aquatic ecology and hydrobiology which involve the study of aquatic organisms and the interactions of these organisms with the abiotic (non-living) environment. While limnology has substantial overlap with freshwater-focused disciplines (such as freshwater biology), it also includes the study of inland salt lakes. A more recent sub-discipline of limnology is termed landscape limnology which involves studies, management, and the conservation of these ecosystems using a landscape perspective, by explicitly examining connections between an aquatic ecosystem and the related watershed. Recently, the need to understand global inland waters as part of the system of the Earth led to the creation of sub-discipline called global limnology which considers processes in inland waters on a global scale, like the role of inland aquatic ecosystems in global biogeochemical cycles.

See als: Aquasphere.

Linseed oil

Linseed oil, also known as flaxseed oil or flax oil (in its edible form), is a colorless- to-yellowish oil obtained from the dried, ripened seeds of the flax lant (*Linum usitatissimum*). The oil is obtained by pressing which is sometimes followed by solvent extraction.

Linseed oil is a drying oil which can polymerize into a solid form. Owing to its polymer-forming properties, linseed oil can be used on its own or blended with combinations of other oils. Linseed oil is a triglyceride (Figure L-2), and it is distinctive for its unusually large amount of alpha-linolenic acid, which has a distinctive reaction with oxygen in air.

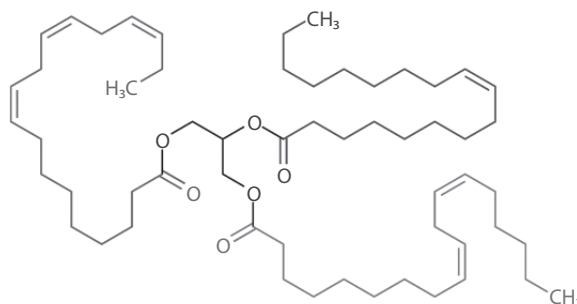


Figure L-2 Example of a complex triglycerides of the type found in linseed oil.

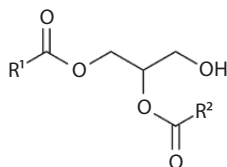
Specifically, the fatty acids in a typical linseed oil are of the following types: (i) the triply unsaturated α -linolenic acid, (ii) the saturated acids palmitic acid and stearic acid, (iii) the monounsaturated oleic acid, and (iv) the doubly unsaturated linoleic acid.

See also: Flax and Flaxseed Oil.

Lipids

Lipid derivatives are diverse in both their respective structures and functions. These diverse compounds that make up the lipid family are so grouped because they are insoluble in water (hydrophobic). They are also soluble in other organic solvents such as ether, acetone, and other lipids. Lipids serve a variety of important functions in living organisms and also act as chemical messengers, serve as valuable energy sources, provide insulation, and are the main components of membranes. Major lipid derivatives include the phospholipids derivatives.

Briefly, the phospholipids are a class of lipids that are a major component of all cell membranes. They can form lipid bilayers because of their amphiphilic characteristic. The structure of the phospholipid molecule generally consists of two hydrophobic fatty acid tails and a hydrophilic head consisting of a phosphate group. The two components are usually joined together by a glycerol ($\text{HOCH}_2\text{CHOHCH}_2\text{OH}$) molecule.



Example of a diglyceride

Liquefaction

Liquefaction is the conversion of a solid feedstock such as biomass into nearly mineral-free hydrocarbon liquids or low-melting solids by a process of direct or indirect hydrogenation at elevated temperatures and pressures and separation of liquid products from residue by either filtration or distillation or both. The production of liquid fuels from biomass is not new and has received considerable attention since the concept does represent alternate pathways to liquid fuels. In fact, the concept is often cited as a viable option for alleviating projected shortages of liquid fuels as well as offering some measure of energy independence for those countries with vast resources of biomass who are also net importers of crude oil.

The process options for biomass liquefaction can generally be divided into four categories: (i) pyrolysis, (ii) solvent extraction, (iii) catalytic liquefaction, and (iv) indirect liquefaction. The final category of direct liquefaction process employs the concept of catalytic liquefaction in which a suitable catalyst is used to add hydrogen to the feedstock. These processes usually require a liquid medium with the catalyst dispersed throughout or may even employ a fixed-bed reactor. On the other hand, the catalyst may also be dispersed within the feedstock whereupon the combined feedstock-catalyst system can be injected into the reactor. Many processes of this type have the advantage of eliminating the need for a hydrogen donor solvent (and the subsequent hydrogenation of the spent solvent), but there is still the need for an adequate supply of hydrogen. The nature of the process also virtually guarantees that the catalyst will be deactivated by the mineral matter in the feedstock as well as by coke lay-down during the process. Furthermore, in order to achieve the direct hydrogenation of the feedstock, the catalyst and the feedstock must be in intimate contact, but if this is not the case, process inefficiency is the general rule.

Liquid Absorption Processes

Liquid absorption processes evolved from dry box processes. They are based on the same reactions as the dry box methods, using a metal oxide to react with hydrogen sulfide to form a metal sulfide compound. These liquid processes were developed to facilitate simple and rapid change out of the media while also enabling the development of continuous processes. They are generally composed of a slurry of active metal oxides suspended in water. The primary metal oxides used are iron oxide and zinc oxide.

Liquid absorption processes (which usually employ temperatures below 50°C , 120°F) are classified either as *physical solvent processes* or *chemical solvent processes*. The former processes employ an organic solvent, and absorption is enhanced by low temperatures, or high pressure, or both. Regeneration of the solvent is often accomplished readily. In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkaline solutions such as amines or carbonates. Regeneration (desorption) can be achieved by use of reduced pressures and/or high temperatures, whereby the acid gases are stripped from the solvent.

See also: Absorption, Gas Cleaning, Gas Processing.

Liquid Biofuels

Fossil fuels applications are linked with current widely held environmental issues, and the decline of fossil fuel resources with environmental penalties has compelled for substitutes and usage of renewable biofuel as energy sources; it has gained a significant importance in last three decades, and the production of fuels from biological resources is proving to be an ecologically viable and sustainable option.

Liquid biofuels include liquid fuels – such as biodiesel and bioethanol – that are produced from various types of biomass, several kinds of biowastes, and agricultural residues, is an ecologically viable and sustainable option. Currently, the most widely used liquid biofuels for transport are ethanol and biodiesel. Ethanol is a type of alcohol that can be produced using any feedstock containing significant amounts of sugar, such as sugar cane or sugar beet, or starch, such as maize and wheat.

There are various ways of producing biofuels, but the processes generally use chemical reactions, fermentation, and heat to break down the starch derivatives, sugar derivatives, as well as other plant-based chemicals. The resulting products are then refined to produce a fuel that cars or other vehicles can use.

See also: Biofuels – Bioalcohol, Biodiesel, Ethanol, Liquid, Liquid Fuels.

Liquid Fuels

Liquid fuels are combustible or energy-generating molecules that can be harnessed to create mechanical energy. It is the fumes of liquid fuels that are flammable instead of the fluid. Most liquid fuels in widespread use are derived from fossil fuel sources, but there are several types derived from non-fossil fuel sources – these are hydrogen, methanol, ethanol, and biodiesel that are derived from non-fossil fuel sources which are also categorized as a liquid fuel.

Biofuel is a generic name for gaseous, liquid, or solid fuels that are not derived from fossil fuels or contain a proportion of non-fossil fuel. For the purposes of this text, the term alternate fuels is used to represent those fuels that are produced from plant sources as well as from other sources such as the organic constituents (predominantly biological in nature) municipal and industrial waste. Thus, biofuels are *bio-materials* that are produced made from renewable biological sources which are now contemplated as grown specifically for the purpose of providing useful heat upon combustion. Biofuels are produced from sources such as: corn, soybeans, flaxseed, rapeseed, sugarcane, palm oil, sugar beet raw sewage, food scraps, animal parts, and rice.

Biofuels are fuels derived from plant materials – and are entering the market, driven by factors such as oil price spikes and the need for increased energy security. Examples of solid biofuels include wood, sawdust, grass cuttings, domestic refuse, charcoal, agricultural waste, non-food energy crops, and dried manure. Biofuels are also known as non-conventional fuels or alternative fuels. Alternative fuels can be classified as any fuel that is not derived from conventional sources like natural gas, crude oil, and coal.

See also: Biodiesel, Ethanol, Liquid Fuels from Biomass, Liquid Fuels from Waste, Liquid Fuels from Wood, Methanol, Propanol and Butanol.

Liquid Fuels from Biomass

Generally, liquid fuels are those fuels (often but not always hydrocarbon derivatives) which flow readily under ambient conditions. Liquid fuels from biomass represent a different class of chemicals.

Alcohols are oxygenate fuels insofar as the alcohol molecule has one or more oxygen, which decreases to the combustion heat. Practically, any of the organic molecules of the alcohol family can be used as a fuel. The alcohols can be used for motor fuels are methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), and butanol ($\text{C}_4\text{H}_9\text{OH}$). However, only methanol and ethanol fuels are technically and economically suitable for internal combustion engines.

Ethanol (ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$), also referred to as bioethanol, is a clear, colorless liquid with a characteristic, agreeable odor. Currently, the production of ethanol by fermentation of corn-derived carbohydrates is the main technology used to produce liquid fuels from biomass resources. Furthermore, among different biofuels, suitable for

application in transport, bioethanol and biodiesel seem to be the most feasible ones at present. The key advantage of bioethanol and biodiesel is that they can be mixed with conventional petrol and diesel respectively, which allows using the same handling and distribution infrastructure. Another important strong point of bioethanol and biodiesel is that when they are mixed at low concentrations ($\leq 10\%$ bioethanol in petrol and $\leq 20\%$ biodiesel in diesel), no engine modifications are necessary.

Ethanol can be blended with gasoline to create E85, a blend of 85% ethanol and 15% gasoline. E85 blends with even higher concentrations of ethanol, E95; pure bioethanol (E100-fuel) has been used mainly in Brazil. More widespread practice has been to add up to 20% to gasoline (E20-fuel or gasohol) to avoid engine changes.

Ethanol has a higher octane number (108), broader flammability limits, higher flame speeds, and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time, and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine.

On the other hand, the disadvantages of ethanol include its lower energy density than gasoline, its corrosiveness, low flame luminosity, lower vapor pressure, miscibility with water, and toxicity to ecosystems.

Ethanol from cellulosic biomass materials (such as agricultural residues, trees, and grasses) is made by first using pretreatment and hydrolysis processes to extract sugars, followed by fermentation of the sugars. Although producing ethanol from cellulosic biomass is currently more costly than producing ethanol from starch crops, several countries (including the United States) have launched biofuels initiatives with the objective of the economic production of ethanol from bio-sources. Researchers are working to improve the efficiency and economics of the cellulosic bioethanol production process.

In the process, the carbohydrate from the biomass into sugar; this is converted to ethanol in a fermentation process that is similar to the process for brewing beer. Typical feedstocks for the process are sugar beets and from molasses and yield are on the order of 72.5 liters of ethanol per ton of sugar cane. Modern crops yield 60 tons of sugar cane per hectare of land. Production of ethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution. Domestic production and use of ethanol for fuel can decrease dependence on foreign oil, reduce trade deficits, create jobs in rural areas, reduce air pollution, and reduce global climate change carbon dioxide buildup.

Ethanol can also be produced by synthesis from the chemical compound ethylene, which is derived from crude oil or natural gas, or by the fermentation of carbohydrates.

Methanol (methyl alcohol, wood alcohol, CH_3OH) is mainly manufactured from natural gas, but biomass can also be gasified to methanol. Methanol can be made with any renewable resource containing carbon such as seaweed, waste wood, and garbage. Methanol is stored and handled like gasoline because it is produced as a liquid. Methanol is currently made from natural gas, but it can also be made from a wide range of renewable biomass sources, such as wood or waste paper.

In comparison to gasoline, ethanol contains 35% oxygen by weight; gasoline contains none. The presence of the oxygen promotes more complete combustion which results in fewer tailpipe emissions. Compared to the combustion of gasoline, the combustion of ethanol substantially reduces the emission of carbon monoxide, volatile organic compounds, particulate matter, and greenhouse gases. However, a unit of ethanol contains approximately 32% less energy than a liter of gasoline. One of the best qualities of ethanol is its octane rating.

Methanol can be used as one possible replacement for conventional motor fuels and has favorable properties. Methanol has been seen as a possible large volume motor fuel substitute at various times during gasoline shortages. It was often used in the early part of the century to power automobiles before inexpensive gasoline was widely introduced. Methanol is poisonous and burns with an invisible flame. Methanol has just like ethyl alcohol a high octane rating, and hence an Otto engine is preferable. If an ignition booster is used, methanol can be used in a diesel engine.

Methanol also offers important emissions benefits compared with gasoline. It can reduce hydrocarbon emissions by 30 to 40% with M85 and up to 80% with M100 fuels. Methanol costs less than gasoline, but has lower energy content. Taking this into account, costs for methanol in a conventional vehicle are slightly higher than those for gasoline. When used in fuel cells, which are considerably more efficient, fuel costs will be lower. Three important points of comparison are emissions, fuel economy, and octane quality.

Methanol and methanol blends have higher octane ratings than gasoline, which reduces engine knock and can produce in higher engine efficiency. The higher octane also gives methanol-fueled vehicles more power and quicker

acceleration. A higher octane rating allows certain engine design parameters, such as compression ratio, and valve timing, to be altered in such ways that fuel economy and power are increased.

E100-fueled and M100-fueled vehicles have difficulty starting in cold weather, but this is not a problem for E85 and M85 vehicles because of the presence of gasoline.

P-Series fuels are a unique blend of natural gas liquids, ethanol, and hydrocarbon derivatives methyl tetrahydrofuran ($\text{CH}_3\text{C}_4\text{H}_7\text{O}$) and are a biomass-derived product. These fuels are clear, colorless liquid blends (octane number: 89 to 93) that are formulated to be used in flexible fuel vehicles. Like gasoline, low vapor pressure formulations are produced to prevent excessive evaporation during summer and high vapor pressure formulations are used for easy starting in the winter. Also, these fuels are at least 60% non-petroleum and the majority of the components that make up P-series fuels come from domestically produced renewable resources.

The P-Series fuels provide significant emissions benefits over reformulated gasoline. Each unit of P-series fuel emits approximately 50% less carbon dioxide, 35 % less hydrocarbon derivatives, and 15% less carbon monoxide than gasoline. The fuel also has 40% less ozone forming potential. The other gasoline-substitute ether, MTBE (methanol tertiary butyl ether), is a petroleum-derived product and is made from isobutene [$(\text{CH}_3)_2\text{CH}=\text{CH}_2$ and methanol]. The P-series fuel emissions are generally below those for reformulated gasoline and are well below federal emissions standards. P-series fuels join the list of alternatives to gasoline that includes ethanol (E85), methanol (M85), natural gas, propane, and electricity.

Biodiesel is the generic name for fuels obtained by esterification of vegetable oil. The esterification can be done either by methanol or by ethanol. Biodiesel can be used in a diesel engine without modification and is a clean burning alternative fuel produced from domestic, renewable resources. The fuel is a mixture of fatty acid alkyl esters made from vegetable oils, animal fats, or recycled greases. Where available, biodiesel can be used in compression-ignition (diesel) engines in its pure form with little or no modifications.

Biodiesel is biodegradable, nontoxic, and essentially free of sulfur and aromatics. It is usually used as a petroleum diesel additive to reduce levels of particulates, carbon monoxide, hydrocarbon derivatives, and air toxics from diesel-powered vehicles. When used as an additive, the resulting diesel fuel may be called B5, B10, or B20, representing the percentage of the biodiesel that is blended with petroleum diesel.

Biodiesel is produced through a process in which organically derived oils are combined with alcohol (ethanol or methanol) in the presence of a catalyst to form the ethyl or methyl ester. The biomass-derived ethyl or methyl esters can be blended with conventional diesel fuel or used as a neat fuel (100% biodiesel). Biodiesel can be made from any vegetable oil, animal fats, waste vegetable oils, or microalgae oils. Soybeans and Canola (rapeseed) oils are the most common vegetable oils used currently.

Biodiesel is usually made from soybean oil or recycled cooking oils. Animal fats, other vegetable oils, and other recycled oils can also be used to produce biodiesel, depending on their availability.

The production of biodiesel from vegetable oil represents another means of producing liquid fuels from biomass, and one which is growing rapidly in commercial importance. Commercially, biodiesel is produced from vegetable oils, including rapeseed, sunflower and soybean oil, and animal fats. These oils and fats are typically composed of C_{14} to C_{20} fatty acid triglycerides (constituting approximately 90 to 95% by weight of the oil). In order to produce a fuel that is suitable for use in diesel engines, these triglycerides are converted to the respective alkyl esters and glycerol by base-catalyzed transesterification with short chain alcohols (generally methanol).

Thus, for every 10 lbs. of biodiesel produced, approximately 1 lb. of glycerol is formed. Glycerol finds application in a wide range of industries (cosmetics, pharmaceuticals, as a plasticizer, etc.), although as biodiesel production grows, new uses will have to be developed to avoid a surplus of glycerol.

Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751) in order to ensure proper performance. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments and biodiesel that meets ASTM D6751 and is legally registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution. Raw vegetable oil cannot meet biodiesel fuel specifications; therefore, it is not registered with the EPA and it is not a legal motor fuel.

A totally different process than that used for biodiesel production can be used to convert biomass into a type of fuel similar to diesel which is known as bio-oil. The process (fast pyrolysis, flash pyrolysis) occurs when solid fuels are heated at temperatures between 350 and 500°C (660 and 930°F) for a short period of time (<2 seconds). The bio-oils currently produced are suitable for use in boilers for electricity generation.

In another process, the feedstock is fed into a fluidized bed (at 450 to 500°C, 845 to 930°F) and the feedstock flashes and vaporizes. The resulting vapors pass into a cyclone where solid particles, char, are extracted. The gas from the cyclone enters a quench tower where they are quickly cooled by heat transfer using bio-oil already made in the process. The bio-oil condenses into a product receiver, and any non-condensable gases are returned to the reactor to maintain process heating. The entire reaction from injection to quenching takes only two seconds.

See also: Alcohols, Biomass, Biofuels, Liquid Fuels From Waste, Synthesis Gas.

Liquid Fuels From Waste

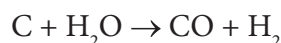
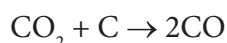
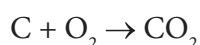
Using ethanol as the example, numerous waste streams could be exploited for ethanol production. They are often inexpensive to obtain, and in many instances, they have a negative value attributable to current disposal costs. Some principal waste streams currently under consideration include mixed paper from municipal solid waste, cellulosic fiber fines from recycled paper mills, as well as various bio-feedstocks.

However, each waste stream has its own unique characteristics, and they generally vary from one source or time to another. Therefore, ethanol or, for that matter, the production of liquid fuels from waste streams is not only feedstock dependent but is also process dependent.

Using the term loosely, the standard way of preparing hydrocarbon liquid fuels from carbonaceous material is to (i) gasify the feedstock to produce synthesis gas and (ii) convert the synthesis gas by the Fischer-Tropsch reaction to hydrocarbon derivatives.

Synthesis gas (syngas) is the name given to a gas mixture that contains varying amounts of carbon monoxide and hydrogen generated by the gasification of a carbonaceous fuel to a gaseous product with a heating value. Examples include (i) steam reforming of natural gas or liquid hydrocarbon derivatives to produce hydrogen and (ii) waste-to-energy gasification processes.

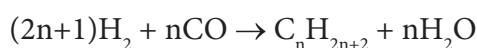
Synthesis gas consists primarily of (predominantly) carbon monoxide and hydrogen and has less than half the energy density of natural gas. Synthesis gas is combustible and often used as a fuel source or as an intermediate for the production of other chemicals. Synthesis gas for use as a fuel is most often produced by gasification of coal or municipal waste mainly by the following paths:



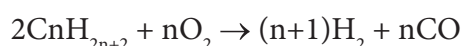
When used as an intermediate in the large scale, industrial synthesis of hydrogen and ammonia, it is also produced from natural gas (via the steam reforming reaction) as follows:



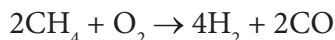
The Fischer-Tropsch synthesis is, in principle, a carbon chain building process, where methylene groups are attached to the carbon chain. The actual reactions that occur have been, and remain, a matter of controversy, as it has been the last century since 1930s.



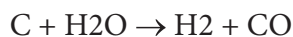
The initial reactants in the above reaction (i.e., CO and H₂) can be produced by other reactions such as the partial combustion of a hydrocarbon derivative:



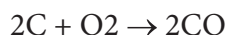
For example (when $n=1$), methane (in the case of gas-to-liquids applications):



Or by the gasification of any carbonaceous source, such as biomass and, in the current context, carbonaceous waste:



The energy needed for this endothermic reaction is usually provided by (exothermic) combustion with air or oxygen:



A modification of this concept involves the proposed addition of addition of hydrogen from a carbon-free energy source, such as solar or nuclear power, during the gasification step. The theoretical concept is a hybrid process insofar as liquid hydrocarbon fuels are proposed to be produced from biomass wherein biomass is the carbon source and hydrogen is supplied from carbon-free energy. Modeling of this biomass-to-liquids process indicates that the concept has the potential to provide the transportation sector for the foreseeable future, using the existing infrastructure.

In addition, although not mentioned because the concept is modeled on the complete gasification of the feedstock, the addition of hydrogen will not only suppress the formation of carbon dioxide but also the formation of other by-products thereby increasing the efficiency of the process. The presence of hydrogen will also reduce the amount of char and tarry by-products which is in complete agreement with the observed beneficial effect of hydroprocesses in petroleum refineries which has been known for decades. The hydrogen and energy balance may be even better if water (also produced during gasification) could be used as the hydrogen source.

The pyrolysis of waste tires is also a source of liquid fuels; the process by which this is achieved is often called thermal depolymerization. This term, however, is more a term of convenience since it is rare that depolymerization, in the true scientific sense, actually occurs.

Thermal depolymerization (TDP) is a term that is used to describe the reduction of complex organic materials into lower-molecular-weight products. Nevertheless, in this context, thermal cracking and catalytic cracking as used in the petroleum industry are examples of thermal depolymerization. The feedstocks for such processes may also include non-oil-based waste products, such as old tires, offal, wood, and plastic. However, the so-called thermal depolymerization process does not in any way mimic the natural geological processes thought to be involved in the production of fossil fuels, such as petroleum and natural gas.

In the thermal depolymerization process, conversion efficiencies can be high but is feedstock dependent. Quantifying the potential amount of product (e.g., biodiesel) can be done on a feedstock carbon compared to product carbon basis, but such estimates are only approximate.

Quantifying the amount of oil which could be produced from tire pyrolysis can be done in a similar manner to quantifying the amount of biodiesel produced from waste vegetable oil. It is simply a case of equating the amount of waste product available to the production yields. In the case of tire pyrolysis, the number of used tires produced each year is well documented. What is less certain, however, is the amount of suitable road transport oil that can be yielded from the pyrolysis process itself.

Another source of waste for the production of liquid fuels is waste cooking oil; usually, biodiesel is the desired product. In fact, waste cooking oil is a valuable asset for conversion to liquid fuels and the quantity of biodiesel which could be produced from waste cooking oil can be quantified in a manner similar to that of biodiesel produced direct from agriculture. The only difference is that rather than calculating crop yields, it is necessary to quantify the amount of waste oil available.

Biodiesel is a light-to-dark-yellow liquid that is immiscible with water and has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point on the order of approximately 150°C (300°F), making it non-flammable. Biodiesel has a density of 0.88 g/cm³. Biodiesel has a viscosity similar to diesel derived from crude

oil (sometimes referred to as petrodiesel to differentiate the different forms of diesel) and can be used as an additive in formulations of diesel to increase the lubricity of pure ultra-low sulfur diesel (ULSD) fuel. Much of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix, in contrast to the “BA” or “E” system used for blends of diesel fuel with ethanol. For example, fuel containing 20% biodiesel is labeled B20 whereas pure biodiesel is referred to as B100.

Biodiesel is a renewable fuel that can be manufactured from algae, vegetable oils, animal fats, or recycled restaurant greases; it can be produced locally in most countries. It is safe, biodegradable, and reduces air pollutants, such as particulates, carbon monoxide, and hydrocarbon derivatives. Blends of 20% biodiesel with 80% petroleum diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems.

Biodiesel is an alternative to petroleum-based diesel, but it is produced from biodegradable materials and can be used as fuel in diesel engines. It can also be used in boilers or furnaces designed to use heating oil or in oil-fueled lighting equipment or used neat (100% biodiesel), or it can be blended with petroleum diesel.

Biodiesel is made by chemically reacting vegetable oil or animal fat (or combinations of oils and fats) with alcohol (usually nearly pure methanol or ethanol) and a catalyst (sodium hydroxide). The chemical reaction converts constituents of the vegetable oil into an ester (biodiesel fuel) and glycerol. Since the biodiesel is less dense than the glycerol, it floats on top of the glycerol and may be pumped off, or the glycerol can be drained off the bottom. The fuel can then be filtered and used in heating or lighting applications. It is possible to use the product in diesel engines without further processing, but caution is advised because of the potential for engine damage, and it is recommended that impurities (unreacted alcohol and sodium hydroxide) are removed by washing.

Almost any variety of oil or grease (from new food-grade vegetable oil to used cooking oil or trap grease to wastewater treatment-plant grease) can be converted and turned into biodiesel. However, the amounts of reactants (oil, methanol, and sodium hydroxide) vary to some degree, depending on what oil is used. The amount of methanol and sodium hydroxide must be sufficient to react with the vegetable oil, but excessive amounts of these reactants should not be used. Just as an engine requires excess air to be sure that all the fuel burns, it takes excess methanol to be sure all of the oil reacts.

The chemistry of biodiesel production is known as transesterification insofar as the process involves reaction of a glyceride-containing plant oil with a short chain alcohol such as methanol or ethanol. The process can be represented simply as:

Vegetable oil → transesterification/methanol → glycerol/methanol + crude biodiesel
 Vegetable oil → transesterification/ethanol → glycerol/ethanol + crude biodiesel
 Glycerol/methanol → refining → glycerol + methanol
 Glycerol/ethanol → refining → glycerol + ethanol
 Crude biodiesel → biodiesel

Animal and plant fats and oils are typically made of triglyceride derivatives which are esters of free fatty acid derivatives with the trihydric alcohol, glycerol. In the transesterification reaction, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. Usually, this reaction will proceed either slowly or not at all. Heat, as well as an acid or base, is used to help the reaction proceed more quickly.

Almost all biodiesel is produced using the base-catalyzed technique as it is the most economical process requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids).

The major steps required to synthesize biodiesel are (i) purification, (ii) neutralization, (iii) transesterification, and (iv) workup.

Purification is required if waste vegetable oil is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. The crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration, but the viscosity of the oil may not allow the drying agent to mix thoroughly.

Neutralization of free fatty acids in which a sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity (in moles) of base required to neutralize the acid is then calculated.

Transesterification in which while adding the base, a slight excess is factored in to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide) is added slowly to the alcohol, and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess is added to drive the reaction to completion. The solution of sodium hydroxide in the alcohol is then added to a warm solution of the waste oil, and the mixture is heated (typically 50°C) for several hours (4 to 8 typically) to allow the transesterification to proceed. A condenser may be used to prevent the evaporative losses of the alcohol. Care must be taken not to create a closed system which can explode.

Workup occurs when the reaction is complete. The glycerol should sink, but when ethanol is used, it is reported that an emulsion often forms. This emulsion can be broken by standing, centrifugation, or the addition of a low-boiling (easily removed) non-polar solvent, decanting, and distilling. The top layer, a mixture of biodiesel and alcohol, is decanted. The excess alcohol can be distilled off, or it can be extracted with water. If the latter, the biodiesel should be dried by distillation or with a drying agent.

The overall process consists of a thermo-chemical conversion of synthesis gas which is then converted to higher-molecular-weight alcohols by a catalytic process after which high purity ethanol is separated by distillation. The process is similar to modern-day methanol and gas-to-liquids processes. The key differentiating factors are the catalysts and their operating parameters.

See also: Alcohols, Biomass, Biofuels, Liquid Fuels From Waste, Synthesis Gas.

Liquid Fuels from Wood

Wood can be used to make both liquid and gaseous fuels. When wood is heated in the absence of air, or with a reduced air supply, it is possible to produce a liquid fuel which can be used in a similar way to conventional oil fuels. It can be used to run internal combustion engines in vehicles or generators. The gas produced from wood is a mixture of hydrogen and carbon monoxide (synthesis gas) which is similar to the coal gas which was made before the arrival of natural gas from the North Sea. This wood gas can be used in internal combustion engines or in gas turbines which can be used to power generators. Although the liquid fuels are rarely produced from wood at present, wood gas is important in other countries for producing electricity in more remote areas.

Processes for making liquid fuels from wood have been understood and available for longer than such fuels have been used in vehicles for transportation. However, the economics of liquid fuels from wood as compared to liquid fuels from fossil fuels have been unfavorable. Nevertheless, the recent phenomenal increases in the cost of gasoline and diesel fuel, that seem to bear little relationship to the increases in petroleum process, has caused a renewed interest in liquid fuels from sources other than petroleum. Wood is a fuel source of interest!

The three approaches that are most promising for making liquid fuels from wood are methanol, ethanol, and diesel fuel, but other liquid fuels from wood are possible. Methanol was the first fuel from wood and is often called wood alcohol. Ethanol has been the focus of research at the Forest Products Laboratory. There has been little attention to diesel fuel from wood, although there has been some research on production from synthesis gas and through utilization of extractable materials from wood.

Liquid fuels that could be suitable for use in transportation vehicles have been made from wood for a long time. Methanol was commonly called wood alcohol, and this term is still used. Cellulose which is the largest wood component could be dissolved in concentrated acid solutions and converted to sugar, a precursor for making ethanol. A dilute sulfuric acid hydrolysis process was used to make ethanol during World War I, and wood hydrolysis received considerable attention in Europe during the period between the World Wars I and II. Wood hydrolysis plants continue to operate in Russia.

However, methanol and ethanol are not the only transportation fuels that might be made from wood. A number of possibilities exist for producing alternatives. The most promising biomass fuels, and closest to being competitive in current markets without subsidy, are (i) ethanol, (ii) methanol, (iii) ethyl-t-butyl ether, and (iv) methyl-t-butyl ether.

Other candidates include isopropyl alcohol, sec-butyl alcohol, t-butyl alcohol, mixed alcohols, and t-amyl methyl ether.

Ethanol or grain alcohol is not restricted to grain as a feedstock. It can be produced from other agricultural crops and lingo-cellulose compounds such as wood. It has often been advocated as a motor fuel, and has been used frequently in times of gasoline scarcity.

Another possibility for oxygenated fuels is methanol. Methanol could conceivably be made from grain, but its most common source is natural gas. Use of natural gas is better for reducing carbon dioxide production in comparison to other fossil fuels, but use of renewable fuels instead of natural gas would be still better. It can be made from coal or wood with more difficulty and lower efficiency than from natural gas.

High octane rating is characteristic of all oxygenated fuels, including ethanol, methanol, ethyl-t-butyl ether, and methyl-t-butyl ether. A large part of the success of ethanol from grain in the current United States mix of motor fuels is its ability to raise octane rating in a 10% mixture of ethanol with 90% gasoline. However, it is the recent phenomenal growth in the use of methyl-t-butyl-ether (MTBE) as an octane enhancer that has captured worldwide attention. MTBE is made by reacting isobutylene with methanol. Ethyl-t-butyl ether (ETBE) is made by using ethanol instead of methanol. Thus, either ethanol or methanol from either grain or wood could be a factor in making t-butyl ether octane enhancers. The characteristics of ethers are generally closer to those of gasoline than those of alcohols.

Ethers are benign in their effect on fuel system materials and are miscible in gasoline; therefore, they are not subject to phase separation in the presence of water, as are methanol and ethanol. Ethers are non-polar. They are of low volatility and thus give low evaporative emissions.

Alternative fuels from wood, as well as grain, have a potential for being competitive with gasoline and diesel motor fuels from petroleum, even without subsidization. Currently, ethanol from grain and a slight amount from wood are competing, but only with a large Federal and some State subsidies. However, environmental and octane-enhancing benefits of ethanol and other oxygenated fuels that may be produced from grain and wood may make them worth more than comparisons on fuel value alone would indicate.

Diesel fuel or gasoline from wood are possibilities through a number of approaches. The one that appears simplest is to use an exudation or gum from a tropical wood species, *Copaifera*, which is said to be directly combustible in a diesel engine. The Fischer-Tropsch pyrolysis process, used successfully for converting coal to synthesis gas in South Africa, could also be used to make synthesis gas from wood. Synthesis gas could then be used to make gasoline or diesel fuel. Or methanol could be produced from wood and then, by a catalyzed reaction known as the Mobil process, be transformed to gasoline.

Although, ideally, there should be additional pilot testing for any process to produce ethanol or methanol from wood commercially, technology for ethanol production has been developed and subjected to some pilot testing. The technology is available for fairly rapid implementation, should the need for alternative fuels become pressing as the result of another global petroleum emergency. Depending on feedstock costs and other variables, ethanol from wood might or might not be able to compete with ethanol from corn. Another important consideration is production and marketing of by-products such as high fructose corn syrup and distillers dry grains from corn and molasses and/or furfural from wood. The two-stage, dilute sulfuric acid hydrolysis process is a possibility for commercial application in producing ethanol from low-grade hardwoods.

In the two-stage hydrolysis process, for every 100 kg of oven-dry wood feedstock, approximately 20 kg carbohydrates suitable for processing to ethanol are obtained from the second stage. There are more carbohydrates derived from the first stage, approximately 24.9 kg, but many of these first-stage carbohydrates are not necessarily fermentable to ethanol.

Ethanol is a possibility if xylose can be fermented to ethanol economically. Fermentation of the xylose and glucose from the first stage could result in almost doubling the ethanol production as compared to only fermenting the glucose from the second stage. Other possible products from the first-stage carbohydrates are single-cell protein, furfural, and feed molasses.

Methanol was once produced from wood as a by-product of charcoal manufacture, but overall yields were low. To produce methanol from wood with a significantly higher yield would require production of synthesis gas in a process similar to that used for production of methanol from coal. Such processes for gasifying wood are less fully developed than the two-stage hydrolysis process for production of ethanol. Another consideration in producing liquid fuels from wood is the amount of wood available to manufacture the fuels.

For converting wood to liquid fuel, the most optimistic assumption normally used is that wood could be converted to liquid fuel in the ratio of BTU in liquid fuel/BTU in wood = 0.5. At least in the short run, it would be difficult to find more than 100 million dry tons of wood per year (1.7 Quads equivalent) for this purpose. This would calculate to be a maximum of 13 billion gallons per year if the output was methanol, and the energy content of a ton of dry wood is assumed to be 17 million BTU. On the order of 11.5 billion gallons per year would be needed if methanol were added to gasoline at the rate of 10% methanol to 90% gasoline.

Projections of wood use for energy to 2010 are modest. Currently, 2.7 Quads of energy are produced from wood. Projections of the total for 2010 are approximately 4.0 Quads. This does not provide for a total growth of even 1.7 Quads. However, if we really want to get serious approximately doing something to deter atmospheric CO₂ accumulation, the availability of wood for energy, including solid as well as liquid fuel, could be increased, up to 10 Quads per year might be very realistic. This runs counter to decreased usage of wood for all purposes, particularly from the National forests, to provide more wilderness, habitat for threatened and endangered species, clean water, and other environmental considerations. However, it must be remembered that, in some cases, more harvesting and clean-up of residues is needed to increase the vigor of forest growth, to protect the forest against wildfire, and to prepare the soil for new growth.

See also: Alcohols, Biomass, Biofuels, Cellulose, Lignin, Lignocellulose, Liquid Fuels From Waste, Synthesis Gas.

Liquid Fuels – Biodiesel

Among the liquid biomass fuels, biodiesel (vegetable oil ester) is noteworthy for its similarity to crude oil-derived diesel fuel, apart from its negligible sulfur and ash content. Bioethanol has only approximately 70% the heating value of crude oil distillates such as gasoline, but its sulfur and ash contents are also low. Both of these liquid fuels have lower vapor pressure and flammability than their crude oil-based competitors – an advantage in some cases (e.g., use in confined spaces such as mines) but a disadvantage in others (e.g., engine starting at cold temperatures).

Currently, the production of ethanol by fermentation of corn-derived carbohydrates is the main technology used to produce liquid fuels from biomass resources. Furthermore, among different biofuels, suitable for application in transport, bioethanol and biodiesel seem to be the most feasible ones at present. The key advantage of bioethanol and biodiesel is that they can be mixed with conventional gasoline and diesel, respectively, which allows using the same handling and distribution infrastructure. Another important strong point of bioethanol and biodiesel is that when they are mixed at low concentrations ($\leq 10\%$ bioethanol in gasoline and $\leq 20\%$ biodiesel in diesel), no engine modifications are necessary.

Alternatively, biomass can be converted into fuels and chemicals indirectly (by gasification to synthesis gas followed by catalytic conversion to liquid fuels) or directly to a liquid product by thermochemical means. Direct thermochemical conversion processes include pyrolysis, liquefaction, and solvolysis. Thermochemical treatment of biomass to produce hydrocarbon derivatives has been studied since the 1930s, and while relatively simple to perform, typically such processes are non-selective, producing a wide range of products.

The production of biodiesel from vegetable oil represents another means of producing liquid fuels from biomass, and one which is growing rapidly in commercial importance. Commercially, biodiesel is produced from vegetable oils, including rapeseed, sunflower and soybean oil, and animal fats. These oils and fats are typically composed of C₁₄ to -C₂₀ fatty acid triglycerides (constituting approximately 90 to 95% by weight of the oil). In order to produce a fuel that is suitable for use in diesel engines, these triglycerides are converted to the respective alkyl esters and glycerol by base-catalyzed transesterification with short chain alcohols (generally methanol).

Thus, for every 10 units of biodiesel produced, approximately 1 unit of glycerol (HOCH₂CHOHCH₂OH) is formed. Glycerol finds application in a wide range of industries (such as cosmetics, pharmaceuticals, and plasticizers).

Liquid Fuels – Ethanol

Ethanol is the predominant fuel produced from crops and has been used as fuel in the United States since at least 1908. Although early efforts to sustain an ethanol program failed, oil supply disruptions in the Middle East and

environmental concerns over the use of lead as a gasoline octane booster renewed interest in ethanol in the late 1970s. At present, extending the volume of conventional gasoline is a significant end use for ethanol, as is its use as an oxygenate. To succeed in these markets, the cost of ethanol must be close to the wholesale price of gasoline, currently made possible by the federal ethanol subsidy. However, in order for ethanol to compete on its own merits, the cost of producing it must be reduced substantially.

The production of ethanol from corn is a mature technology that holds much potential. Substantial cost reductions may be possible, however, if cellulose-based feedstocks are used instead of corn. Producers are experimenting with units equipped to convert cellulose-based feedstocks, using sulfuric acid to break down cellulose and hemicellulose into fermentable sugar. Although the process is expensive at present, advances in biotechnology could decrease conversion costs substantially. The feed for all ethanol fermentations is sugar – traditionally a hexose (a six-carbon or “C6” sugar) such as those present naturally in sugar cane, sugar beet, and molasses. Sugar for fermentation can also be recovered from starch, which is actually a polymer of hexose sugars (*polysaccharide*).

Biomass, in the form of wood and agricultural residues such as wheat straw, is viewed as a low-cost alternative feed to sugar and starch. It is also potentially available in far greater quantities than sugar and starch feeds. As such, it receives significant attention as a feed material for ethanol production. Like starch, wood and agricultural residues contain polysaccharides. However, unlike starch, while the cellulose fraction of biomass is principally a polymer of easily fermented C6 sugars, the hemicellulose fraction is principally a polymer of C5 sugars; with quite different characteristics for recovery and fermentation, the cellulose and hemicellulose in biomass are bound together in a complex framework of crystalline organic material known as lignin.

These differences mean that recovery of these biomass sugars is more complex than recovery of sugars from a starch feed. Once recovered, fermentation is also more complex than a simple fermentation of C6 sugars. The current focus focuses on the issues of releasing the sugars (hydrolysis) and then fermenting as much of the C6 and C5 sugars as possible to produce ethanol.

There are several different methods of hydrolysis: (i) concentrated sulfuric acid, (ii) dilute sulfuric acid, (iii) nitric acid, and (iv) acid pretreatment followed by enzymatic hydrolysis.

Ethanol is produced from the fermentation of sugar by enzymes produced from specific varieties of yeast. The five major sugars are the five-carbon xylose and arabinose and the six-carbon glucose, galactose, and mannose. Traditional fermentation processes rely on yeasts that convert six-carbon sugars to ethanol. Glucose, the preferred form of sugar for fermentation, is contained in both carbohydrates and cellulose. Because carbohydrates are easier than cellulose to convert to glucose, the majority of ethanol currently produced in the United States is made from corn, which produces large quantities of carbohydrates. Also, the organisms and enzymes for carbohydrate conversion and glucose fermentation on a commercial scale are readily available.

The conversion of cellulosic biomass to ethanol parallels the corn conversion process. The cellulose must first be converted to sugars by hydrolysis and then fermented to produce ethanol. Cellulosic feedstocks (composed of cellulose and hemicellulose) are more difficult to convert to sugar than are carbohydrates. Two common methods for converting cellulose to sugar are dilute acid hydrolysis and concentrated acid hydrolysis, both of which use sulfuric acid.

Dilute acid hydrolysis occurs in two stages to take advantage of the differences between hemicellulose and cellulose. The first stage is performed at low temperature to maximize the yield from the hemicellulose, and the second, higher temperature stage, is optimized for hydrolysis of the cellulose portion of the feedstock. Concentrated acid hydrolysis uses a dilute acid pretreatment to separate the hemicellulose and cellulose. The biomass is then dried before the addition of the concentrated sulfuric acid. Water is added to dilute the acid and then heated to release the sugars, producing a gel that can be separated from residual solids. Column chromatographic is used to separate the acid from the sugars.

Both the dilute and concentrated acid processes have several drawbacks. Dilute acid hydrolysis of cellulose tends to yield a large amount of by-products. Concentrated acid hydrolysis forms fewer by-products, but for economic reasons, the acid must be recycled. The separation and concentration of the sulfuric acid adds more complexity to the process. The concentrated and dilute sulfuric acid processes are performed at high temperatures (100 to 220°C, 212 to 430°F) which can degrade the sugars, reducing the carbon source and ultimately lowering the ethanol yield. Thus, the concentrated acid process has a smaller potential for cost reductions from process improvements such as acid recovery and sugar yield for the concentrated acid process could provide higher efficiency for both technologies.

Another approach involves countercurrent hydrolysis, a two-stage process. In the first stage, cellulose feedstock is introduced to a horizontal co-current reactor with a conveyor. Steam is added to raise the temperature to 180°C

(no acid is added at this point). After a residence time of approximately 8 minutes, during which some 60% of the hemicellulose is hydrolyzed, the feed exits the reactor. It then enters the second stage through a vertical reactor operated at 225°C (440°F). Very dilute sulfuric acid is added to the feed at this stage, where virtually all of the remaining hemicellulose and, depending on the residence time, anywhere from 60% to all of the cellulose is hydrolyzed. The countercurrent hydrolysis process offers higher efficiency (and, therefore, cost reductions) than the dilute sulfuric acid process. This process may allow an increase in glucose yields to 84%, an increase in fermentation temperature to 55°C (131°F), and an increase in fermentation yield of ethanol to 95%.

The greatest potential for ethanol production from biomass, however, lies in enzymatic hydrolysis of cellulose. The enzyme cellulase, now used in the textile industry to stone wash denim and in detergents, simply replaces the sulfuric acid in the hydrolysis step. The cellulase can be used at lower temperatures, 30 to 50°C, which reduces the degradation of the sugar. In addition, process improvements now allow simultaneous saccharification and fermentation (SSF). In the saccharification and fermentation process, cellulase and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step. Once the hydrolysis of the cellulose is achieved, the resulting sugars must be fermented to produce ethanol. In addition to glucose, hydrolysis produces other six-carbon sugars from cellulose and five-carbon sugars from hemicellulose that are not readily fermented to ethanol by naturally occurring organisms. They can be converted to ethanol by genetically engineered yeasts that are currently available, but the ethanol yields are not sufficient to make the process economically attractive. It also remains to be seen whether the yeasts can be made hardy enough for production of ethanol on a commercial scale.

A large variety of feedstocks is currently available for producing ethanol from cellulosic biomass. The materials being considered can be categorized as agricultural waste, forest residue, and energy crops. Agricultural waste available for ethanol conversion includes crop residues such as wheat straw, corn stover (leaves, stalks, and cobs), rice straw, and bagasse (sugar cane waste). Forestry waste includes underutilized wood and logging residues; rough, rotten, and salvable dead wood; and excess saplings and small trees. Energy crops, developed and grown specifically for fuel, include fast-growing trees, shrubs, and grasses such as hybrid poplars, willows, and switchgrass.

Briefly, corn stover is the leaves and stalks of field crops, such as corn (maize), sorghum or soybean that are commonly left in a field after harvesting the grain. It is similar to straw, the residue left after any cereal grain or grass has been harvested at maturity for its seed. It can be directly grazed by cattle or dried for use as fodder; stover has attracted some attention as a potential fuel source, and as a biomass feedstock for fermentation or as a feedstock for ethanol production from cellulose.

Although the choice of feedstock for ethanol conversion is largely a cost issue, feedstock selection has also focused on environmental issues. Materials normally targeted for disposal include forest thinnings collected as part of an effort to improve forest health, and certain agricultural residues, such as rice straw. Also, forest residues represent an opportunity to decrease the fire hazard associated with the dead wood present in many forests. Small quantities of forest thinnings can be collected at relatively low cost, but collection costs rise rapidly as quantities increase.

Agricultural residues, in particular corn stover, represent a tremendous resource base for biomass ethanol production. Agricultural residues, in the long term, would be the sources of biomass that could support substantial growth of the ethanol industry. At conversion yields of around 60 to 100 gallons per dry ton, the available corn stover inventory would be sufficient to support 7 to 12 billion gallons of ethanol production per year.

Dedicated energy crops such as switchgrass, hybrid willow, and hybrid poplar are another long-term feedstock option. Switchgrass is grown on a 10-year crop rotation basis, and harvest can begin in year 1 in some locations and year 2 in others. Willows require a 22-year rotation, with the first harvest in year 4 and subsequent harvests every 3 years thereafter. Hybrid poplar requires 6 years to reach harvest age in the Pacific Northwest, 8 years in the Southeast, Southern Plains, and South Central regions, and 10 years in the Corn Belt, Lake States, Northeast, and Northern Plains regions.

The use of cellulosic biomass in the production of ethanol also has environmental benefits. Converting cellulose to ethanol increases the net energy balance of ethanol compared to converting corn to ethanol. The net energy balance is calculated by subtracting the energy required to produce a gallon of ethanol from the energy contained in a gallon of ethanol (approximately 76,000 Btu). Corn-based ethanol has a net energy balance of 20,000 to 25,000 Btu per gallon, whereas cellulosic ethanol has a net energy balance of more than 60,000 Btu per gallon. In addition, cellulosic ethanol use can reduce greenhouse gas emissions. Cellulosic ethanol can produce an 8 to 10% reduction in greenhouse gas emissions when used in E10 and a 68 to 91% reduction when used in E85.

Liquid Fuels – Methanol

Methanol is a colorless, odorless, and nearly tasteless alcohol and is also produced from crops and is also used as a fuel. Methanol, like ethanol, burns more completely but releases as much or more carbon dioxide than its gasoline counterpart. The balance is often seen as the various bi-processes that draw carbon dioxide from the atmosphere so there is no net modern release, as there is for fossil fuels.

Methanol and other chemicals were routinely extracted from wood in the 19th century and in the early 20th century. However, the original route for methanol recovery from biomass was quite different to current routes. Methanol was originally recovered from wood as a by-product of charcoal manufacture, and was often called *wood alcohol*. Pyrolysis (heating wood in the absence of air) to above 270°C (>520°F) in a retort causes thermal cracking or break-down of the wood and allows much of the wood to be recovered as charcoal. The watery condensate leaving the retort contained methanol, among other compounds. In 1923, commercial production of methanol from synthesis gas by a catalytic process was commenced. Now, almost all of the methanol used worldwide comes from the processing of natural gas.

In general, methanol production from natural gas feed consists of three steps: (i) generation of synthesis gas – in the case of natural gas feed, synthesis gas production consists of converting methane (CH_4) into carbon monoxide (CO) and hydrogen (H_2) via steam reforming, (ii) synthesis gas upgrading – primarily removal of carbon dioxide, plus any contaminants such as sulfur, and (iii) methanol synthesis and purification – reacting the carbon monoxide, hydrogen, and steam over a catalyst in the presence of a small amount of carbon dioxide and at elevated temperature and pressure. The methanol synthesis is an equilibrium reaction, and excess reactants must be recycled to optimize yields.

Modern methods proposed for the production of methanol from biomass involve the conversion of the biomass to a suitable synthesis gas, after which processing steps are similar to those developed for methanol from natural gas. However, the gasification techniques proposed are still at a relatively early stage of development using biomass feed and the methods are based on similar techniques used widely already with natural gas as feed.

Before biomass can be gasified, it must be pre-treated to meet the processing constraints of the gasifier. This typically involves size reduction, and drying to keep moisture contents below specific levels. Thereafter, biomass gasification involves heating biomass in the presence of low levels of oxygen (i.e., less than required for complete combustion to carbon dioxide and water). Above certain temperatures, the biomass will break down into a gas stream and a solid residue. The composition of the gas stream is influenced by the operating conditions for the gasifier, with some gasification processes more suited than others to producing a gas for methanol production. In particular, simple gasification with air creates a synthesis gas stream that is diluted with large quantities of nitrogen. This nitrogen is detrimental to subsequent processing to methanol, and so techniques using indirect gasification or an oxygen feed are preferred. For large-scale gasification, pressurized systems are considered to be more economic than atmospheric systems.

Once the economic optimum synthesis gas is available, the methanol synthesis takes place. This typically uses a copper-zinc catalyst at temperatures of 200 to 280°C and pressures of 50 to 100 atmospheres. The crude methanol from the synthesis loop contains water produced during synthesis as well as other minor by-products. Purification is achieved in multistage distillation, with the complexity of distillation dictated by the final methanol purity required.

Liquid Fuels – Propanol and Butanol

Propanol and butanol are considerably less toxic and less volatile than methanol. In particular, butanol has a high flashpoint (35°C; 95°F), which is a benefit for fire safety, but may be a difficulty for starting engines in cold weather.

The fermentation processes to produce propanol and butanol from cellulose are fairly tricky to execute, and the *Clostridium acetobutylicum* currently used to perform these conversions produces an extremely unpleasant smell, and this must be taken into consideration when designing and locating a fermentation plant. This organism also dies when the butanol content of whatever it is fermenting rises to 7%. For comparison, yeast dies when the ethanol content of its feedstock hits 14%. Specialized strains can tolerate even greater ethanol concentrations – so-called turbo yeast can withstand up to 16% ethanol. However, if ordinary *Saccharomyces* yeast can be modified to improve its ethanol resistance, scientists may yet one day produce a strain of the Weizmann organism with a butanol resistance higher than the natural boundary of 7%. This would be useful because butanol has a higher energy density than

ethanol, and because waste fiber left over from sugar crops used to make ethanol could be made into butanol, raising the alcohol yield of fuel crops without there being a need for more crops to be planted.

Liquid-Liquid Extraction

Liquid-liquid extraction is the commonest of the solvent extraction processes and is often the second choice, after distillation, when considering alternatives for separating large volumes of liquid mixtures. If the feedstock contains only a small amount of impurity and the impurity has a higher boiling point than the rest of the mixture, liquid-liquid extraction can even become preferable to distillation on an energy consumption basis. This is because distillation would have to vaporize almost all of the feed to recover the small amount of impurity.

Extraction could directly remove the minor component. Liquid extraction is widely used in the petroleum refining, chemical, and nuclear industries for the purification of aqueous and non-aqueous liquid process streams. However, the current use in waste minimization applications is largely confined to removal and recovery of organic materials from aqueous waste streams.

See also: Solvent Extraction, Supercritical Fluid Extraction.

Lithosphere

The lithosphere is outermost shell of the Earth that is composed of the crust and the portion of the upper mantle that behaves elastically on time scales of thousands of years or greater, defined on the mineralogy. The lithosphere is subdivided into tectonic plates which are the uppermost part of the lithosphere that chemically reacts to the atmosphere, the hydrosphere, and the biosphere through the soil-forming process (called the pedosphere). There are two types of lithosphere which are (i) the oceanic lithosphere, which is associated with the oceanic crust and exists in the oceanic basins and has a density of approximately of approximately 2.9 grams per cubic centimeter, and (ii) the continental lithosphere, which is associated with the continental crust and has a on the order of 2.7 grams per cubic centimeter.

The oceanic lithosphere consists mainly of a mafic mantle (mafic: an adjective describing a silicate mineral or igneous rock that is rich in magnesium and iron) crust and ultramafic mantle (over 90% mafic) and is denser than continental lithosphere. It thickens as it ages and moves away from the mid-ocean ridge. This thickening occurs by conductive cooling, which converts hot asthenosphere into lithospheric mantle. It was less dense than the asthenosphere for tens of millions of years, but after this becomes increasingly denser. The gravitational instability of mature oceanic lithosphere has the effect that when tectonic plates come together, oceanic lithosphere invariably sinks underneath the overriding lithosphere. New oceanic lithosphere is constantly being produced at mid-ocean ridges and is recycled back to the mantle at subduction zones, so oceanic lithosphere is much younger than its continental counterpart. The oldest oceanic lithosphere is approximately 170 million years old compared to parts of the continental lithosphere which are billions of years old.

On the other hand, the continental lithosphere (also called the continental crust) is the layer of igneous, sedimentary rock that forms the continents and the continental shelves. This layer consists mostly of granitic rock. Continental crust is also less dense than oceanic crust, although it is considerably thicker. Approximately 40% of the surface of the Earth is covered by continental crust, but continental crust makes up approximately 70% v/v of the crust of the Earth. The continental crust is believed to have been derived from the fractional differentiation of oceanic crust over geologic time (hundreds of millions of years) and was primarily a result of volcanism and subduction.

The lithosphere is underlain by the asthenosphere, which is the weaker, hotter, and deeper part of the upper mantle. The lithosphere-asthenosphere boundary is defined by a difference in response to stress in which the lithosphere remains rigid for long periods of geologic time in which it deforms elastically and through brittle failure. On the other hand, the asthenosphere undergoes considerable deformation and accommodates strain through this deformation.

Logging Residue

The various types of logging residue include stumps, tops, limbs, and unutilized cull trees. Stump residue, the part of the tree that is lower than the cutting point and thus left after the harvesting operation, is generally not available

commercially since the cost of obtaining the stump or root biomass is likely prohibitive. Tops refer to the tops of the trees that are either broken during harvesting or are cut off the central stem of the tree due to a merchantability standard. Limbs refer to the branches of the trees.

Cull trees are the trees that cannot be used to produce saw logs due to defects, rot, or form. Some cull trees are used as pulpwood, and others are left unutilized as a part of logging residue. Tops, limbs, and unutilized cull trees are the logging residue that is potentially available as biomass for energy production or chemical extraction.

See also: Biomass, Logs And Woodchips, Mill Residue, Wood.

Logs and Woodchips

Log-fired heating conjures up images of open fires and log stoves for many people, but there are also sophisticated, controllable, log-boilers available which can provide central heating and hot water. Logs are readily available in many areas where there are existing markets for domestic fuel wood. Logs should be well seasoned before burning to ensure the most efficient combustion, and should ideally be stored under cover in a well ventilated log store for a year or more.

Logs are ideal for providing heat for domestic buildings and are suitable for heating loads of up to around 50 kW. Log heating systems do require manual stoking once a day, which makes logs less convenient than more automated heating systems such as woodchips and pellets. Log-fired systems are available with outputs greater than 500 kW to heat larger building such as village halls; however, these larger systems will require more frequent fueling.

Wood chips are made from whole trees, branch wood, or coppice products which have been mechanically shredded by a chipping machine. For some types of boilers, the wood needs to have been air-dried before chipping, or the chips dried before burning. Wood chips are a bulky fuel and sufficient storage and delivery access needs to be considered when designing a heating system.

The use of a timber resource for local woodchip heating would provide a valuable economic return and stimulate the rural economy. Woodchip systems can provide automated, clean, and convenient heating for larger domestic properties with outputs of 20 to 30 kW, up to large-scale systems for hospitals, factories, schools, and district heating schemes with heating loads in the megawatt range. Woodchips can also be used to fuel combine heat and power plants in which the heat produced during electricity generation is used to provide hot water, and is not lost as in conventional power stations.

See also: Biomass, Wood.

Low-Btu Gas

Low-BTU gas consisting of a mixture of carbon monoxide, hydrogen, and some other gases with a heating value typically less than 300 Btu/scf (Btu/ft³, Btu ft⁻³).

For production of low Btu gases, air is typically used as a combusting (or, gasifying) agent. Since air, instead of pure oxygen, is used, the product gas inevitably contains a large concentration of undesirable constituents like nitrogen or nitrogen-containing compounds. Therefore, it unavoidably results in a low heating value of 150-300 Btu/scf. Sometimes, this type of gasification of coal may be carried out in-situ, i.e., underground, where mining of coal by other techniques is not economically favorable. For such in-situ gasification, low-Btu gas may be a desired product.

Low-Btu gas contains five principal components with around 50% v/v nitrogen, some quantities of hydrogen and carbon monoxide (combustible), carbon dioxide, and some traces of methane. The presence of such high contents of nitrogen makes the product gas be classified as "low Btu." The other two non-combustible components (CO₂ and H₂O) further lower the heating value of the product gas. The presence of these components limits the applicability of low-Btu gas to chemical synthesis. The two major combustible components are hydrogen and carbon monoxide, whose ratio varies depending on the gasification conditions employed. One of the most undesirable components is hydrogen sulfide (H₂S) whose content is proportional to the sulfur content of the original coal. It must be removed by gas cleaning procedures before product gas can be used for other useful purposes such as further processing and upgrading.

See also: Gasification, Gasification of Biomass.

Lower Explosive Limit

The lower explosive limit is the lower explosive limit of a gas or vapor at ordinary (ambient) temperature is the percent by volume of the gas vapor in air and is the lower limit at which the gas explodes or inflames. Conversely, the upper explosive limit of a gas or vapor at ordinary (ambient) temperature is the percent by volume of the gas vapor in air and is the upper limit at which the gas explodes or inflames (Table L-5).

Table L-5 Examples of the lower and upper explosive limits of selected chemicals in air.

Chemical	LEL	UEL
1,3-Butadiene	2.0	12.0
1-Butene	1.6	10.0
Benzene	1.3	7.9
Butane	1.8	8.4
Carbon Monoxide	12.5	74.0
Carbonyl Sulfide	12.0	29.0
Cyclohexane	1.3	7.8
Cyclopropane	2.4	10.4
Dimethyl Ether	3.4	27.0
Ethane	3.0	12.4
Ethanol	3.3	19.0
Ethylene	2.7	36.0
<i>Chemical</i>	<i>LEL</i>	<i>UEL</i>
<i>Chemical</i>	<i>LEL</i>	<i>UEL</i>
Heptane	1.1	6.7
Hexane	1.2	7.4
Hydrogen	4.0	75.0
Hydrogen sulfide	4.0	44.0
Isobutane	1.8	8.4
Isobutylene	1.8	9.6
Methane	5.0	15.0
Methanol	6.7	36.0
Methyl mercaptan	3.9	21.8
Propylene	2.4	11.0
Toluene	1.2	7.1
Xylene	1.1	6.6

Similarly, the lower flammability limit is the minimum concentration by volume of a combustible substance that is capable of propagating a flame under specified conditions and the upper flammability limit is the maximum concentration by volume of a combustible substance that is capable of continued propagation of a flame under the specified conditions.

However, these limits are to be used as a guide only since, under a variety of other circumstances, methane and the other hydrocarbon constituents of natural gas are explosive and flammable.

See also: Explosive Limits, Lower Flammability Limit, Upper Explosive Limit, Upper Flammability limit.

Lower Flammability Limit

Flammability limits, also called flammable limits, or *explosive limits* give the proportion of combustible gas in a mixture, between which limits this mixture is flammable. Gas mixtures consisting of combustible, oxidizing, and inert gases are only flammable under certain conditions.

The lower flammability limit is the minimum concentration by volume of a combustible substance that is capable of propagating a flame under specified conditions. The lower flammability limit (LFL), usually expressed in volume per cent, is the lower end of the concentration range of a flammable solvent at a given temperature and pressure for which air/vapor mixtures can ignite. The upper flammability limit (UFL) (upper explosive limit) gives the richest flammable mixture. An increase in the proportion of inert gas in a mixture raises the lower flammability limit.

The flammability range is delineated by the upper and lower flammability limit. Outside this range of air/vapor mixtures, the mixture will not ignite (unless heated). The lower flammability limit decreases with increasing temperature – a mixture that is below its lower flammability limit at a given temperature may ignite if heated sufficiently.

The lower flammability limit is typically close to the saturated vapor concentration at the flash point; however, due to differences in technique between measuring lower flammability limit and the various flash points (open/closed cup as well as different apparatus), some spread in the data usually exists.

See also: Lower Explosive Limit, Upper Explosive Limit, Upper Flammability Limit.

Lower Heating Value

The lower heating value (net calorific value, net CV, or LHV) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C or another reference state) and returning the temperature of the combustion products to 150°C.

The lower heating value assumes all the water component is in vapor state at the end of combustion (in product of combustion), as supposed to higher heating value which that assumes all the water component in liquid form of the combustion gas.

The lower heating value assumes that the latent heat of vaporization of water in the fuel and the reaction products is not recovered. It is useful in comparing fuels where condensation of the combustion products is impractical, or heat at a temperature below 150°C cannot be put to use.

See also: Low-Btu Gas, Low Heat Content Gas.

Low-Heat Content Gas

Low-heat content gas (low-BTU gas) is a mixture of coal gases containing nitrogen with a heat content of 100-200 Btu/ft³ produced in gasification processes using air as the oxygen source. It is the air-blown form of producer gas.

During the production of coal gas by oxidation with air, the oxygen is not separated from the air and, as a result, the gas product invariably has a low heat-content (150 to 300 Btu/ft³). Low heat-content gas is also the usual product of in situ gasification of coal which is used essentially as a method for obtaining energy from coal without the necessity of mining the coal, especially if the coal cannot be mined or of mining is uneconomical.

Several important chemical reactions, and a host of side reactions, are involved in the manufacture of low heat-content gas under the high temperature conditions employed. Low heat-content gas contains several components, four of which are always major components present at levels of at least several percent; a fifth component, methane, is marginally a major component.

The nitrogen content of low heat-content gas ranges from somewhat less than 33% v/v to slightly more than 50% v/v and cannot be removed by any reasonable means; the presence of nitrogen at these levels makes the product gas *low heat-content* by definition. The nitrogen also strongly limits the applicability of the gas to chemical synthesis. Two other noncombustible components (water, H_2O , and carbon dioxide, CO_2) further lower the heating value of the gas; water can be removed by condensation and carbon dioxide by relatively straightforward chemical means.

The two major combustible components are hydrogen and carbon monoxide; the H_2/CO_2 ratio varies from approximately 2:3 to approximately 3:2. Methane may also make an appreciable contribution to the heat content of the gas. Of the minor components, hydrogen sulfide is the most significant and the amount produced is, in fact, proportional to the sulfur content of the feed coal. Any hydrogen sulfide present must be removed by one, or more, of several procedures.

Low heat-content gas is of interest to industry as a fuel gas or even, on occasion, as a raw material from which ammonia, methanol, and other compounds may be synthesized.

See also: Low-Btu Gas, Lower Heating Value.

Low-Temperature Char

Char is produced by the low-temperature (approximately 650°C; 1,200°F) carbonization of coal. The two major properties of low-temperature char which make it a useful fuel are its clean, smokeless combustion and its relatively high reactivity. Current environmental regulations may make the smokeless quality of char even more desirable. Furthermore, carbonization leads to an appreciable loss of sulfur as well as undesirable trace elements, so that the char is a *cleaner* fuel than the original coal.

The fact that the low-temperature char is quite reactive means that ignition and burning will be efficient, a desirable property for fuel to be used in open-bed furnaces.

Another potential advantage of low-temperature char involves its production from very low-rank fuels, such as lignite or brown coal. These abundant fuels have low heat values and high water contents, but low-temperature carbonization can convert these fuels to a high-heat (per unit weight) char. Thus, there is the potential for conversion of these coals at the mine site by means of volatile gases (or chars) to generate electricity while the premium quality solid fuel (char) is transported elsewhere for use.

As active thermal decomposition proceeds and is followed by secondary degasification, the solid residues are progressively aromatized and homogenized by growth of graphitic lamellae which are increased in size by heating to higher temperatures. However, the properties of the chars which give an indication of lamellar growth and graphitic ordering (as the more familiar stacks of lamellae) do not change to any marked degree until temperatures on the order of 500 to 550°C (930 to 1020°F) are reached. In addition, the ultrafine pore structure of the coal may be retained until temperatures on the order of 650 to 700°C (1,200 to 1,290°F) are reached.

Lurgi Combined Reforming Process

The Lurgi combined reforming process was originally developed for large-scale methanol production, and it is with an example from this application that it is described here. In the context of the production of liquid fuels, it is suitable as a building block for the methanol-to-gasoline (MTG) process or the olefins-to-gasoline, and distillates (MOGD) process. For the high-pressure Synthol process, carbon dioxide needs to be purged from the system. The conventional tubular steam reforming process as used for methanol syngas production produces a hydrogen/carbon monoxide ratio of over 4 and a stoichiometric ratio of 2.6 to 2.9 (i.e., a hydrogen-rich gas) depending on the quality of the natural gas feedstock.

Auto-thermal reforming or partial oxidation produces carbon monoxide-rich gases with a hydrogen/carbon monoxide ratio in the range 1.5 to 3.5 and a stoichiometric number of approximately around 1.8.

Approximately half the feed is processed in the tubular primary reformer. The other half, together with the primary reformer effluent, is auto-thermally reformed with pure oxygen in the secondary reformer. Besides matching hydrogen-rich and carbon monoxide-rich process steps to produce an optimum stoichiometric ratio, the Combined Reforming process has beneficial effects such as:

The methane slip of the overall reforming process is governed by the temperature of the secondary reformer that is not subject to the same limitations of tube metallurgy as the tubular reformer. The combined process can thus provide a lower methane slip.

Less synthesis gas of the optimized quality is required per ton of methanol, reducing both the syngas compressor load and the capital cost of the synthesis unit.

The operating temperature of the primary reformer need no longer be chosen to minimize methane slip. The reformer can be operated under mild conditions. The higher operating pressure thus possibly enables the syngas compressor load to be further reduced.

The reduced throughput through the primary reformer together with the lower operating temperature combine to reduce the tubular reformer to approximately 25% of the size of that required for the single-stage process. This reduces the stack gas losses referred to earlier by the same amount.

One feature common to all Fischer-Tropsch processes is the inherent lack of selectivity. The actual selectivity will depend on the desired product slate as well as on the catalyst and the operating conditions. In all cases, however, substantial quantities of gaseous hydrocarbon derivatives including methane are produced.

In principle, it is desirable to recycle these gaseous hydrocarbon derivatives to produce more synthesis gas. On the other hand, it is necessary to provide a purge of inert gases, principally argon and nitrogen. The other aspect of selectivity that requires recognition is that a proportion of higher-molecular-weight products, including waxes, is produced and may require hydrotreating for conversion to a saleable product.

The Syntroleum process is a gas-to-liquids technology that has been in use for several decades. A major advantage is that the process uses compressed air instead of pure oxygen to facilitate the conversion reaction, substantially reducing the capital costs and vastly improving the safety of the process plants.

See also: Gasification, Gasification of Biomass.

Lurgi Dry Ash Gasifier

The Lurgi dry ash gasifier is a relatively high-pressure, moderate-temperature moving bed gasifier that is typically used for the production of gas from coal but lends itself to the production of gas from biomass.

There are several reaction zones in the gasifier. Devolatilization, including the vaporization of coal moisture, occurs at the top where the incoming coal is heated by the rising hot gases. Further down where the coal char reaches temperatures of 650 to 815°C (1,200 to 1,500°F), the gasification reactions proceed. Temperatures in the bottom combustion zone, where the coal burns to supply heat for the endothermic gasification reactions, are kept below the ash melting point, which may vary from approximately 980 to 1,370°C (1,800 to 2,500°F) depending on the feedstock. Biomass feedstocks would not require such severe temperatures.

As for moving bed gasifiers, the Lurgi gasifier does not readily handle fines, and caking or swelling coals generally require an oxidative pretreatment or internal agitation to prevent plugging and resultant excessive pressure drops. The coal is crushed and screened to between 3 and 40 mm, and the fines are removed and used for raising steam in pulverized coal boilers. If the coal is very friable, the fines content may exceed plant fuel requirements and must be disposed of or sold. Predrying the coal is not necessary; lignite with moisture contents up to 35% may be used directly. Ash contents up to 35% or more are also not a problem, although the poorer heat transfer characteristics of ash may require increased steam rates to prevent clinkering. The sized coal is introduced through the coal lock hopper into the reactor.

Coal residence time within the gasifier is approximately one hour. The ash is withdrawn through the ash lock hopper at the bottom. Heat recovery in this counterflow system is good; the ash is cooled to approximately 400 to 500°C (750 to 930°F) by the incoming steam/oxygen mixture, while the off gases are cooled to 200 to 540°C depending on the moisture in the coal.

Much of the steam introduced into the gasifier is used to control the temperature in the combustion zone, with up to 50% of the steam passing through the system unreacted. High steam concentrations do, however, serve to shift the equilibrium of the carbon-steam and the gas shift reactions to promote hydrogen formation. The intermediate gasification zone temperature results in some methane formation, although much of the methane in the off gas probably results from coal pyrolysis in the devolatilization zone. Tars and oils are also released in this zone and exit with the off gases from which they are later removed by washing with water in the scrubber/cooler.

See also: Gasification, Gasification of Biomass.

Lurgi Process

Lurgi GMBH is currently involved in the design and supply of synthesis gas production units for two major synfuel projects – one based on the Sasol Synthol process and the other using the Shell SMDS synthesis. There is a substantial difference in the hydrogen/carbon monoxide ratios required by the two processes, and this has led to the selection of different syngas production routes.

As an example of a fixed-bed process, the Lurgi process was developed in Germany before World War II and is a process that is adequately suited for large-scale commercial production of synthetic natural gas. The older Lurgi process is a dry ash gasification process which differs significantly from the more recently developed slagging process. The dry ash Lurgi gasifier is a pressurized vertical kiln which accepts crushed ($1/4 \times 1.75$ inches., 6×44 mm) noncaking coal and reacts the moving bed of coal with steam and either air or oxygen.

The feedstock is gasified at 350 to 450 psi, and devolatilization takes place in the temperature range 615 to 760°C (1,140 to 1,400°F), and the residence time in the reactor is approximately 1 hour. Hydrogen is supplied by injected steam, and the necessary heat is supplied by the combustion of a portion of the product char. The revolving grate, located at the bottom of the gasifier, supports the bed of coal, removes the ash, and allows steam and oxygen (or air) to be introduced.

The product gas has high methane content relative to the products from non-pressurized gasifier units. With oxygen injection, the gas has a heat content of approximately 450 Btu/ft³. The crude gas which leaves the gasifier contains tar, oil, phenols, ammonia, coal fines, and ash particles. The steam is first quenched to remove the tar and oil, and, prior to methanation, part of the gas passes through a shift converter and is then washed to remove naphtha and unsaturated hydrocarbon derivatives; a subsequent step removes the acid gases. The gas is then methanated to produce a high heat-content pipeline quality product.

The Wellman Galusha process – also a fixed-bed process – has been in commercial use since the early decades of the 20th century. The two types of gasifiers, the standard type and the agitated type and the rated capacity of an agitated unit may be 25% or more higher than that of a standard gasifier of the same size. In addition, an agitated gasifier is capable of treating volatile caking bituminous coals.

The gasifier is water-jacketed, and, therefore, the inner wall of the vessel does not require a refractory lining. Agitated units include a varying speed revolving horizontal arm which also spirals vertically below the surface of the coal bed to minimize channeling and to provide a uniform bed for gasification. A rotating grate is located at the bottom of the gasifier to remove the ash from the bed uniformly. Steam and oxygen are injected at the bottom of the bed through tuyeres. Crushed coal is fed to the gasifier through a lock hopper and vertical feed pipes. The fuel valves are operated so as to maintain a relatively constant flow of coal to the gasifier to assist in maintaining the stability of the bed and, therefore, the quality of the product gas.

See also: Fixed Bed Process, Gasification, Gasifiers, Lurgi Dry Ash Gasifier, Lurgi Slagging Gasifier.

Lurgi Slagging Gasifier

The Lurgi slagging gasifier (slagging Lurgi gasifier) is an improved version of the Lurgi dry ash gasifier. In the gasifier, the temperature of the combustion zone is kept higher than the ash fusion point by using a smaller amount of steam. The ash is removed from the bottom as slag.

The slagging gasifier is based on the original Lurgi dry ash gasifier, but was intended to improve upon it in the following respects: (i) produce non-leachable vitreous slag rather than dry ash, (ii) improve specific reactor throughput, (iii) increase fines content acceptable in feed, (iv) reduce steam consumption and consequent gas condensate production, (v) recycle tars to extinction, and (vi) increase carbon monoxide and hydrogen (CO/H_2) yields.

In the process, the feedstock is introduced at the top of the water-cooled and refractory-lined gasifier via a lock hopper system. The gasifier is provided with a motor-driven coal distributor/mixer to stir and evenly distribute the incoming coal mixture, which then gradually descends through several process zones. The feedstock at the top of the bed is dried and devolatilized. The descending feedstock is transformed into char, and then passes into the gasification (reaction) zone. Below this zone, oxygen and steam are introduced into the gasifier vessel through side-wall-mounted tuyeres (lances) at the combustion zone, where any remaining char is burned out and slag formation occurs. Slag is withdrawn from the slag pool by means of an opening in the hearth plate at the bottom of the gasifier vessel. The slag flows downward into a quench chamber and lock hopper in series. The pressure differential between the quench chamber and gasifier regulates the flow of slag between the two vessels.

The product gas exits the gasifier at approximately 450°C (840°F) through an opening near the top of the gasifier vessel and passes into a water quench vessel and a boiler feed water preheater designed to lower the temperature to approximately 150°C (300°F). Entrained solids and soluble compounds mixed with the exiting liquid are sent to a gas-liquor separation unit. Soluble hydrocarbons such as tars, oils, and naphtha are recovered from the aqueous liquor and recycled to the top of the gasifier and/or reinjected at the tuyeres.

The main advantage of this gasifier over the conventional dry ash gasifier is that the yield of carbon monoxide and hydrogen is high and the coal throughput increases many times; also, steam consumption is minimized.

See also: Fixed Bed Process, Gasification, Gasifiers, Lurgi Dry Ash Gasifier, Lurgi Slagging Gasifier.

Lye Treating Process

Typically, the term lye is a metal hydroxide that is obtained by leaching wood ashes, or it is a strong alkali which is soluble producing. Lye most commonly refers to sodium hydroxide (NaOH), but has also been used to refer to potassium hydroxide (KOH).

Thus, lye treating is a process for removing acidic constituents from liquid fuels and other products. The process is carried out in continuous treaters, which essentially consist of a pipe containing baffles or other mixing devices into which the oil and lye solution are both pumped. The pipe discharges into a horizontal tank where the lye solution and oil separate. Treated oil is withdrawn from near the top of the tank; lye solution is withdrawn from the bottom and recirculated to mix with incoming untreated oil. A lye-treating unit may be incorporated as part of a processing unit; for example, the overhead from a bubble tower may be condensed, cooled, and passed immediately through a lye-treating unit. Such a unit is often referred to as a worm-end treater since the unit is attached to the particular unit as a point beyond the cooling coil or cooling worm.

Caustic solutions ranging from 5 to 20% w/w are used at 20 to 45°C (70 to 110°F) and 5 to 40 psi. High temperatures and strong caustic are usually avoided because of the risk of color body formation and stability loss. Caustic-product treatment ratios vary from 1:1 to 1:10.

M85

M85 is an alcohol fuel mixture containing 85% v/v methanol and 15% v/v gasoline by volume. Methanol is typically made from natural gas, but can also be derived from the fermentation of biomass (such as wood, hence wood alcohol). Because it is easier to transport natural gas to a distant market by converting it to methanol, which is a liquid at ordinary temperatures and pressures, than by chilling and liquefying it or by building a long pipeline, some crude oil-exporting countries are looking at exporting their waste natural gas (which they currently dispose of by flaring) by converting it to methanol.

There have been efforts to introduce M85 into various fuel markets, notably in California, but there is no nationwide transportation network in place for this as a bulk fuel (on the scale of gasoline, diesel fuel, or natural gas) yet. There are still not very many M85 stations in the United States. However, only relatively small changes need to be made to a gasoline fueling station (such as linings and seals in tanks, pumps, and dispensers) in order to handle M85, compared to the completely new construction needed to handle compressed natural gas (CNG), liquefied natural gas (LNG), or liquefied crude oil gas (LPG), so M85 capability can be added in quickly if local governments, consumers (usually fleets), and retailers decide to develop a market.

Alcohol fuels, such as M85, are perhaps the least distinguishable from gasoline in how they are purchased and used, which should ease acceptance. The fuel system of a car or truck only needs to be slightly changed (somewhat different materials, bigger fuel injectors, and a fuel composition sensor) in order for it to run on M85, and recently, automakers have been offering M85 vehicles at no extra cost over their gasoline counterparts (or even for slightly less money), though at present, automakers seem to be more interested in ethanol-gasoline blends (such as E85).

Most M85 vehicles are flex-fuel vehicles, which means that any mixture of M85 and gasoline in the fuel tank can be used by the engine – a fuel-composition sensor tells the engine computer what percentage of methanol is in the fuel, and it adjusts the injectors and ignition accordingly. Thus, an M85 vehicle is a gasoline vehicle if M85 is not available.

Methanol is more corrosive than gasoline (though it is less toxic and not carcinogenic); this is why an automaker needs to change some of the materials in the fuel-handling systems of both the vehicle and the refueling station to materials that can withstand attack by the fuel. Special oil additives are necessary in order to protect the engine. Also, because the mixture of air to fuel is much richer than gasoline (approximately 8 to 1 by weight, compared to approximately 14 to 1 for gasoline), there is more liquid fuel available to wash oil off of cylinder walls during a cold start.

The richer fuel/air mixture needed by methanol also means that a given volume of gasoline will take you approximately 70% farther than the same tank full of M85; most automakers have at least partially compensated for this by putting a larger fuel tank in their M85 vehicles.

The reason that methanol is most commonly used in a mixture with 15% v/v gasoline is to correct for two disadvantages of pure methanol: (i) a methanol flame is colorless, so gasoline is added to give the flame some color so rescuers can tell if a fire is present should an M85 vehicle get into a crash, and (ii) methanol, being a pure chemical compound, has a single boiling point, so that it can cause cold-start problems in cold weather, or vapor lock in hot.

Gasoline, being a mixture of compounds with different boiling points, always has some components that will remain in the liquid phase and vaporize at a given temperature, so adding it to methanol confers this flexibility on the M85 mixture. As a result, some manufacturers recommend mixing additional gasoline with M85 in the extremely cold weather of northern winters.

See also: Alcohols, Methanol.

Macroalgae

Macroalgae, or seaweeds as they are sometimes called, are also loosely defined as algae that are visible to the naked eye.

Among renewable energy sources, biomass represents the most ready to be implemented on a large scale without any environmental or economic penalty. The photosynthetic efficiency of aquatic biomass results to be much higher (generally 6 to 8%, average) than that of terrestrial (approximately 2%). This makes the former more adaptable for an enhanced carbon dioxide fixation to afford a high biomass production. Aquatic biomass presents an easy adaptability to grow in different conditions, both in fresh-water or marine-water, and in a wide enough range of pH.

Macroalgae are not microalgae or phytoplankton, though the spore stages of several species have been misidentified as species of phytoplankton in the past. Some macroalgae consist of many cells, while some microalgae consist of a single cell, but this is not always the case. Several macroalgae are single-celled, including *Acetabularia* and *Caulerpa*.

Seaweeds are primitive forms of plants, but because they lack vascular tissue, they are definitely algae. Macroalgae species are split into three groups based on their photosynthetic pigments: Phaeophyta (the browns), Rhodophyta (the reds) and Chlorophyta (the greens). Macroalgae, like seaweed, is not as widely used in the production of biodiesel. Microalgae have much more oil than macroalgae, and it is much faster and easier to grow.

Macroalgae are extensively grown and used as food in Asiatic countries, or as source of chemicals. They are usually collected from natural water basins where they are seasonally available. Only recently they have been considered for energy production.

The pond culture of algae presents the advantage of assimilating carbon dioxide emitted by electric power plants, using wastewater that may supply the amount of required nutrients. Either marine microalgae or seaweed could be used for solar energy conversion and biofuel production. Microalgae have received so far more attention with respect to macroalgae as agents for enhanced carbon dioxide fixation due to their facile adaptability to grow in ponds or bioreactors and the extended knowledge on several strains used for fish feeding.

In fact, macroalgae have enormous potential to be the best source of biomass for biofuel. Growing macroalgae in land-based ponds and boosting the growth with carbon dioxide, can be a major source of the algae biomass for biofuels applications. Using carbon dioxide to boost the growing can increase the yield. Macroalgae are the optimal source for second-generation bioethanol, due to (i) high in carbohydrates/polysaccharides and thin cellulose walls, (ii) high yield per growing area, (iii) grown on non-agriculture land, (iv) do not use fresh water, and (v) consumes large amounts of carbon dioxide while growing.

See also: Biomass, Microalgae.

Maize

Maize, also known as corn, is a cereal grain that was first domesticated by the indigenous people in southern Mexico approximately 10,000 years ago.

The crop is a feedstock for the production of biofuel due to the starch content and the comparatively easy conversion of the starch to ethanol. Unlike sugarcane, in which squeezed sugar water can be directly fermented, the corn starch must be converted using alpha and gluco-amylase enzymes to convert the starch to simple sugars. Cellulosic feedstocks are even more recalcitrant and require time and energy to convert to simple sugars.

The life cycle analysis (LCA) of ethanol production from corn grain has yielded a net energy ratio that represents a 20 to 45% positive energy balance in producing ethanol from corn. Environmental issues in corn production revolve around erosion, pesticide use, and nutrient use. Pesticides and nutrients have the potential to contaminate surface and ground water. Soil erosion has led to loss of topsoil and polluted streams and river systems with silt.

See also: Corn.

Manufactured Gas

Manufactured gas is a fuel-gas mixture made from other solid, liquid, or gaseous materials, such as crude oil, coal, coke, or biomass and should not be confused with natural gas. The principal types of manufactured gas are retort coal gas, coke oven gas, water gas, carbureted water gas, producer gas, oil gas, reformed natural gas, and reformed propane or liquefied petroleum gas (LPG). Several processes for making substitute natural gas (SNG) from coal have been developed. Most of the manufactured gas, as it fits into the context of this book, is produced by any one of three processes which, at the present time, find limited use but are still active processes on some areas, and these are: (i) coal carbonization process, (ii) the carbureted water gas process, and (iii) oil gas process.

The *coal carbonization process* was the primary commercial mode of manufacturing gas from ca 1816 to 1875. After 1875, newer processes and technologies gradually replaced coal carbonization. Coal gas was produced through the distillation of bituminous coal in heated, anaerobic vessels called retorts. In this process, coal was broken down into its volatile components through the action of heat in an anaerobic environment. During the retorting phase, approximately 40% w/w of the coal is converted into volatile gases and liquids while the remainder of the coal is converted into solids, primarily coke.

From the retort, some of the gaseous products are condensed (to liquids) and others remain in the gaseous state. The liquids (also called *liquors*) consist of water and coal tar. The products remaining in the gaseous phase are cooled to produce additional coal tar after which the gas is cooled further to remove any other non-gaseous impurities, such as ammonia and sulfur compounds. These are removed by washing the gas in water and by running the gas through beds of moist lime or moist iron oxides. After this final purification process, the coal gas is sent to storage.

The *carbureted water gas process* consists of enriching a form of coal gas, known as water gas (blue gas), to increase the heat content. Thus, by injecting oil into a vessel containing heated water gas, the oil and vapor combined form a gaseous fuel with a thermal content of approximately 300-350 Btu/ft³. Typically, a carbureted water gas plant consists of a brick-lined, cylindrical, steel vessel, the generator, the carburetor (carbureted), and a super-heater. As the gas exits the generator, it is passed into the carburetor where the oil is introduced into the vapor.

The *oil gas process* is similar to carbureted water gas process but consists of steam-cracking the oil in a steam environment to produce the raw gas rather than by distilling coal. From the generator, the gas is passed to a vaporizer, where it is enriched with additional injections of oil and then routed through a super heater. After exiting the super heater, the gas is scrubbed and processed for distribution in much the same way as was carbureted water gas. Many of the same waste products associated with the production of coal gas, notably tars containing polynuclear aromatic hydrocarbons (PNAs, or polyaromatic hydrocarbons, PAHs) were also generated during gas manufacture.

Material Balance

On any process, it is necessary to understand the concept of material balance. Material balance (mass balance) is an application of conservation of mass an expression for conservation of mass governed by the observation that the amount of mass leaving a control volume is equal to the amount of mass entering the volume minus the amount of mass accumulated in the volume.

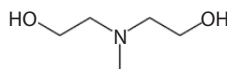
$$M_{\text{original}} = M_{\text{remaining}} + M_{\text{removed}}$$

Furthermore, the pressures measured over time can be used to estimate the volume of hydrocarbon derivatives in place.

By accounting for material entering and leaving a system, mass flows can be identified which might have been unknown, or difficult to measure without this technique. The exact conservation law used in the analysis of the system depends on the context of the problem, but all revolve around mass conservation insofar as matter cannot be created spontaneously or be destroyed.

MDEA

Methyl diethanolamine is a clear, colorless, or pale yellow liquid with an ammonia-like odor. It is miscible with water, alcohol, and benzene. Methyl diethanolamine is also known as N-Methyl diethanolamine and more commonly as MDEA. It has the formula $\text{CH}_3\text{N}(\text{C}_2\text{H}_4\text{OH})_2$ and is a tertiary amine:



The alkanolamine derivatives and their respective aqueous solutions will absorb carbon dioxide and hydrogen sulfide at lower temperatures and release the acid gases at higher temperatures. This forms the basis for processes which separate carbon dioxide and hydrogen sulfide from gas streams.

Methyldiethanolamine is an alkanolamine used in gas treating and hydrogen sulfide enrichment units for selectively removing hydrogen sulfide from gas streams containing carbon dioxide. These units will, in most cases, permit 60 to 80% of the carbon dioxide to remain in the treated gas stream. Methyldiethanolamine is also used in natural gas plants for the bulk removal of carbon dioxide while producing a gas stream containing 0.25 grains hydrogen sulfide/100 ft³. Bulk carbon dioxide removal can be realized with methyldiethanolamine when the carbon dioxide/hydrogen sulfide ratio ranges from 100 to 1,000.

Similar compounds are monoethanolamine (MEA, $\text{HOCH}_2\text{CH}_2\text{NH}_2$), a primary amine, and diethanolamine (DEA, $\text{HOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$), a secondary amine, both of which are also used for in amine (olamine) gas treating units.

See also: Gas Cleaning, MEA.

MEA

Mono-ethanolamine (2-aminoethanol, ethanolamine, and abbreviated as ETA or MEA) is an organic compound that is both a primary amine (due to an amino group in the molecule) and a primary alcohol (due to the hydroxyl group in the molecule):



Ethanamine (mono-ethanolamine)

Like other amines, monoethanolamine is a weak base as well as being a toxic, flammable, corrosive, colorless, viscous liquid with an odor similar to that of ammonia.

The alkanolamines and their aqueous solutions will absorb carbon dioxide and hydrogen sulfide at lower temperatures and release the acid gases at higher temperatures. This forms the basis for processes which separate carbon dioxide and hydrogen sulfide from gas streams.

Methyldiethanolamine is an alkanolamine used in gas treating and hydrogen sulfide enrichment units for selectively removing hydrogen sulfide from gas streams containing carbon dioxide. These units will, in most cases, permit 60 to 80% of the carbon dioxide to remain in the treated gas stream. Methyldiethanolamine is also used in natural gas plants for the bulk removal of carbon dioxide while producing a gas stream containing 0.25 grains hydrogen sulfide/100 scf. Bulk carbon dioxide removal can be realized with methyldiethanolamine when the carbon dioxide/hydrogen sulfide ratio ranges from 100 to 1,000.

Similar compounds are monoethanolamine (MEA, $\text{HOCH}_2\text{CH}_2\text{NH}_2$), a primary amine, and diethanolamine (DEA, $\text{HOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$), a secondary amine, both of which are also used for in amine (olamine) gas treating units.

See also: Gas Cleaning, MDEA.

Mechanical Energy

Mechanical energy is the energy that is possessed by an object due to its motion or due to its position. Mechanical energy can be either (i) kinetic energy, which is energy of motion or (ii) potential energy, which is stored energy of position.

In the physical sciences, mechanical energy is the sum of the kinetic energy and the potential energy and is the energy associated with the motion and position of an object usually in some force field (such as a gravitational field). Mechanical energy (and also the thermal energy) can be separated into two categories which are (i) transient energy and (ii) stored energy. Transient energy is energy in motion, that is, energy being transferred from one place to another, while stored energy is the energy contained within a substance or object. Transient mechanical energy is commonly referred to as work, while stored mechanical energy exists in one of two forms which are (i) kinetic energy or (ii) potential energy.

More specifically, potential energy is the energy stored in an object subjected to a conservative force. Common types include the gravitational potential energy of an object that depends on its mass and its distance from the center of mass of another object. On the other hand, kinetic energy is the energy stored in an object because of its motion which depends on the speed of an object and is the ability of a moving object to do work on other objects when it collides with them.

The principle of conservation of mechanical energy states that if an isolated system is subject only to conservative forces, the mechanical energy is constant. However, if an object moves in the opposite direction of a conservative net force, the potential energy will increase, and if the speed of the object changes, the kinetic energy of the object also changes. In all real systems, however, non-conservative forces, such as frictional, will be present, but if they are of negligible magnitude, the mechanical energy changes little and its conservation is a useful approximation. In elastic collisions, the kinetic energy is conserved, but in when the collisions are non-elastic, some of the mechanical energy may be converted into thermal energy.

A modern wind turbine is an energy-converting machine to convert the kinetic energy of wind into mechanical energy and in turn into electrical energy. In the recent decades in the latter part of the 20th century, it has been estimated that advances in aerodynamics, structural dynamics, and micrometeorology may contribute to a 5% annual increase in the energy yield of wind turbines. Various wind turbine concepts have been developed and built for maximizing the wind energy output, minimizing the turbine cost, and increasing the turbine efficiency and reliability.

See also: Turbine, Wind Energy, Wind Turbines.

Medium-Btu Gas

Medium-BTU gas consists of a mixture of methane, carbon monoxide, hydrogen and various other gases with a heating value in the range of 300-700 Btu/scf.

In the production of medium-Btu gas, pure oxygen rather than air is used as combusting agent, which results in an appreciable increase in the heating value by approximately 300 to 400 Btu/ft³. The product gas predominantly contains carbon monoxide and hydrogen with some methane and carbon dioxide. It is primarily used in the synthesis of methanol, higher-molecular-weight hydrocarbon derivatives via Fischer-Tropsch synthesis, and a variety of other chemicals. It can also be used directly as a fuel to generate steam or to drive a gas turbine. The H₂/CO ratio in medium-Btu gas varies from 2:3 (CO-rich) to more than 3:1 (H₂-rich). The increased heating value is attributed to higher contents of methane and hydrogen as well as to lower concentration of carbon dioxide, besides the absence of nitrogen in the gasifying agent.

See also: Gasification, Gasification of Biomass, Medium Heat Content Gas.

Medium Heat Content Gas

Medium heat-content gas (*medium BTU gas*) has a heating value in the range 300 to 550 Btu/ft³ and the composition is much like that of low heat-content gas, except that there is virtually no nitrogen. The primary combustible gases in medium heat-content gas are hydrogen and carbon monoxide. Medium heat-content gas is considerably more

versatile than low heat-content gas; like low heat-content gas, medium heat-content gas may be used directly as a fuel to raise steam, or used through a combined power cycle to drive a gas turbine, with the hot exhaust gases employed to raise steam, but medium heat-content gas is especially amenable to synthesize methane (by methanation), higher hydrocarbon derivatives (by Fischer-Tropsch synthesis), methanol, and a variety of synthetic chemicals.

The reactions used to produce medium heat-content gas are the same as those employed for low heat-content gas synthesis, the major difference being the application of a nitrogen barrier (such as the use of pure oxygen) to keep diluent nitrogen out of the system.

In medium heat-content gas, the H_2/CO ratio varies from 2:3 C to 3:1 and the increased heating value correlates with higher methane and hydrogen contents as well as with lower carbon dioxide contents. Furthermore, the very nature of the gasification process used to produce the medium heat-content gas has a marked effect upon the ease of subsequent processing. For example, the CO_2 -acceptor product is quite amenable to use for methane production because it has (i) the desired hydrogen to carbon monoxide (H_2/CO) ratio just exceeding 3:1, (ii) an initially high methane content, and (iii) relatively low water and carbon dioxide contents. Other gases may require appreciable shift reaction and removal of large quantities of water and carbon dioxide prior to methanation.

See also: Medium Btu Gas.

Membrane

Membranes are fabricated in relatively small modules; for larger capacity, more modules are added. Cost is therefore virtually linear with capacity, making them more competitive at lower capacities. The design of membrane systems involves a tradeoff between pressure drop (or diffusion rate) and surface area, as well as between product purity and recovery. As the surface area is increased, the recovery of fast components increases; however more of the slow components are recovered, which lowers the purity.

The main gas separation methods are liquefaction/distillation, absorption, adsorption, and membrane-based processes. Membrane separation technologies are rapidly emerging as the preferred separation technology, particularly portable skid-mounted and packaged field processing units. Though, current membrane processes may be costly in some applications, they may be the only method for practical use in natural gas cleanup.

Until recently, the use of *membranes* for gas separation has been limited to carbon dioxide removal. Improvements in membrane technology have now made membranes competitive in other applications in the natural gas area. New membrane materials and configurations exhibit superior performance and offer improved stability against contaminants found in natural gas. The new membranes are targeted at three separations: nitrogen, carbon dioxide/hydrogen sulfide, and natural gas liquids. The process uses a two-step membrane system design; the methane-selective membranes do not need to be operated at low temperatures, and capital and operating costs are within economically acceptable limits.

New membranes have been developed for the gas industry. For example, the membranes allow permeation of condensable vapors, such as C_{3+} hydrocarbon derivatives, aromatics, and water vapor, while rejecting the non-condensable gases, such as methane, ethane, nitrogen, and hydrogen. During the past 15 years, more than 50 systems have been installed in the chemical process industry worldwide. The main applications are nitrogen removal, recovery of natural gas liquids, and dew-point control for associated natural gas and fuel gas conditioning for gas turbines and engines.

In another process, a membrane-based process for upgrading natural gas that contains C_{3+} hydrocarbon derivatives and/or acid gas is described. The conditioned natural gas can be used as fuel for gas-powered equipment, including compressors, in the gas field or the processing plant. Optionally, the process can be used to produce natural gas liquids.

See also: Gas Cleaning, Membrane Processes, Membrane Systems, Ultrafiltration and Microfiltration.

Membrane Permeation

Membrane permeation is the selective diffusion of molecules through a solid polymer film and is also called pervaporation or perstraction when applied to liquid feeds. In fact, the membrane permeation process is a simple

application of selective diffusion through a permeable solid barrier. In its simplest form, the permeable solid barrier separates two chambers, one of which contains the feed stream at higher pressure and the other the product stream, which has diffused through the barrier to a lower pressure.

The concept can be applied to either liquid or gaseous feed mixtures but has found most of its commercial application to date in gas separation processes. In a similar manner to reverse osmosis, the feedstock stream is applied to one side of a solid polymer membrane and the flow of individual components of a feed through the solid polymer film is based on the concentration difference between the upstream and downstream sides of the film for each dissolved component.

For gas streams feedstocks, the concentrations of the components of the gas stream dissolved in the two sides of the membrane are a function of the partial pressure of each of the components in the feedstock and in the product stream. For liquid feedstocks, the downstream concentration is maintained at a low value by either (i) applying a vacuum or a sweep gas to the downstream side of the membrane or (ii) sweeping the downstream surface with a miscible, but easy to separate, solvent. The first configuration, pervaporation, is more common than the second configuration (perstraction). For liquid permeation, the concentrations of the feedstock components in the upstream surface of the membrane are a function of their concentrations in the feed liquid and their solubility in the membrane polymer.

See also: Gas Cleaning, Membrane Processes, Reverse Osmosis, Ultrafiltration and Microfiltration.

Membrane Processes

Membrane processes commonly used for alternative energy systems are reverse osmosis, ultrafiltration, and microfiltration. Permeation and electrodialysis are also finding increasing use. With the exception of permeation, which is still considered a developing technology, all the above are commercial processes. These processes make use of a thin membrane barrier which can be produced with properties that vary over a wide spectrum. The membrane is essentially solid for reverse osmosis, permeation, and electrodialysis; it is porous with continuous discrete holes for microfiltration. Ultrafiltration membranes can be of either type depending on the application.

Generally, the processes are defined by the apparent pore size of the membrane barrier that is employed. This apparent pore size is reported for measured experimental diffusion rates even when it is known that no continuous pores or holes through the membrane exist because the form of the diffusion equations is the same for solid membranes and for porous membranes. The pore size reported for the solid barrier is that which will give the same flow rate for a given pressure drop through a membrane which does have continuous pores.

As they apply to alternative energy systems, membranes were (and still are) used for gas separation has been limited to carbon dioxide removal. Improvements in membrane technology have now made membranes competitive in other applications in the natural gas area. New membrane materials and configurations exhibit superior performance and offer improved stability against contaminants found in natural gas. The new membranes are used in processes for (i) nitrogen removal, (ii) carbon dioxide removal, (iii) hydrogen sulfide removal, and (iv) the removal of higher-molecular-weight hydrocarbon derivatives, also referred to as gas liquids and which includes the C2 to C5 hydrocarbons. The process uses a two-step membrane system design; the methane-selective membranes do not need to be operated at low temperatures, and capital and operating costs are within economically acceptable limits.

Gas permeation membranes are usually made with vitreous polymers that exhibit good diffusional selectivity. However, for separation to be effective, the membrane must be very permeable with respect to the contamination to be separated, which passes through the membrane driven by pressure difference, and it must be relatively impermeable to methane.

Membrane separation processes are designed to process a wide range of feedstocks and offer a simple solution for removal and recovery of higher-boiling hydrocarbon derivatives (natural gas liquids) from natural gas. The separation process is based on high-flux membranes that selectively permeates higher-boiling hydrocarbon derivatives (compared to methane) and are recovered as a liquid after recompression and condensation. The residue stream from the membrane is partially depleted of higher-boiling hydrocarbon derivatives, and is then sent to sales gas stream. Gas permeation membranes are usually made with vitreous polymers that exhibit good selectivity, but, to be effective, the membrane must be very permeable with respect to the separation process.

Membrane systems are very versatile and are designed to process a wide range of feed conditions. Gases can be separated by taking advantage of the difference in rates of diffusion through membranes. Gases that diffuse faster (including hydrogen) become the permeate stream and are available at low pressure, whereas the slower-diffusing gases become the non-permeate and leave the unit at a pressure close to the pressure of the feedstock at entry point. Membrane systems contain no moving parts or switch valves and have potentially high reliability. The major threat is from components in the gas (such as aromatics) that attack the membranes, or from liquids, which plug them.

With very compact footprint and low weight, these systems are well suited for offshore applications. New membranes allow permeation of condensable vapors, such as C_{3+} hydrocarbon derivatives, aromatics, and water vapor, while rejecting the non-condensable gases, such as methane, ethane, nitrogen, and hydrogen. The main applications are nitrogen removal, recovery of natural gas liquids, and dew-point control for associated natural gas and fuel gas conditioning for gas turbines and engines. There is also a membrane-based process for upgrading natural gas that contains C_{3+} hydrocarbon derivatives and/or acid gas is described. The conditioned natural gas can be used as fuel for gas-powered equipment, including compressors, in the gas field or the processing plant. Optionally, the process can be used to produce natural gas liquids.

Until recently, the use of membranes for gas separation has been limited to carbon dioxide removal. Improvements in membrane technology have now made membranes competitive in other applications in the natural gas area. New membrane materials and configurations exhibit superior performance and offer improved stability against contaminants found in natural gas.

New membranes have been developed for the gas industry. For example, the membranes allow permeation of condensable vapors, such as C_{3+} hydrocarbon derivatives, aromatics, and water vapor, while rejecting the non-condensable gases, such as methane, ethane, nitrogen, and hydrogen. During the past 15 years, more than 50 systems have been installed in the chemical process industry worldwide. The main applications are nitrogen removal, recovery of natural gas liquids, and dew-point control for associated natural gas and fuel gas conditioning for gas turbines and engines.

In another process, a membrane-based process for upgrading natural gas that contains C_{3+} hydrocarbon derivatives and/or acid gas is described. The conditioned natural gas can be used as fuel for gas-powered equipment, including compressors, in the gas field or the processing plant. Optionally, the process can be used to produce natural gas liquids.

See also: Gas Cleaning, Membrane Permeation, Microfiltration, Reverse Osmosis, Ultrafiltration.

Mercaptans

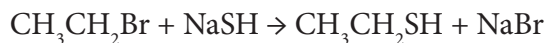
A mercaptan (thiol) is a compound that contains the functional group composed of a sulfur atom and a hydrogen atom ($-SH$), being the sulfur analogue of an alcohol group ($-OH$). This sulfur-containing functional group is referred to either as a *thiol group* or a *sulphydryl group*. More traditionally, thiols are often referred to as *mercaptans*. Since sulfur and oxygen belong to the same periodic table group, they share some similar chemical bonding properties. Like alcohol, in general, the deprotonated form RS^- (thiolate) is more chemically reactive than the protonated thiol form (RSH).

Many thiols are colorless liquids having an odor that is often strong and objectionable, particularly the low-molecular-weight thiols.

Natural gas distributors add various forms of pungent thiols, usually ethanethiol (C_2H_5SH), to natural gas, which is naturally odorless, so that leaks can be easily detected. However, not all thiols have unpleasant odors. For example, grapefruit mercaptan, a monoterpenoid thiol, is responsible for the characteristic scent of grapefruit.

Thiols have lower boiling points than the corresponding alcohols and are less soluble in water and other polar solvents than alcohols of similar molecular weight. The S-H bond in the thiols has a lower dipole moment as compared to the O-H bond. Thiols show little association by hydrogen bonding, with both water molecules and among themselves. As a result, thiols are as soluble and have similar boiling points to the less polar isomeric sulfides.

The methods used in making thiols are analogous to those used to make alcohols and ethers. Thus, thiols are formed when a halogeno-alkane is heated with a solution of sodium hydrosulfide when heated in aqueous ethanol:

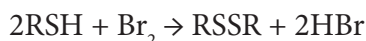


In addition, disulfides can be readily reduced by reducing agents such as lithium aluminum hydride in dry ether to form two thiols derivatives. Thus:

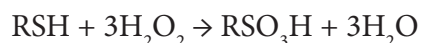


The chemistry of thiols is thus related to the chemistry of alcohols: thiols form thioethers, thioacetals, and thioesters, which are analogous to ethers, acetals, and esters. Furthermore, a thiol group can react with an alkene (olefin) to create a thioether.

The sulfur atom of a thiol is nucleophilic and, in the presence of a base, a thiolate anion is formed. The group and its corresponding anion are readily oxidized by reagents such as bromine to give an organic disulfide:



Oxidation by more powerful reagents such as sodium hypochlorite or hydrogen peroxide yield sulfonic acids (RSO_3H):



Mercury

Mercury, also called quicksilver, is a heavy, silvery metal that is one of six chemical elements that are liquid at or near-liquid at room temperature and pressure. With a melting point of -38.8°C (-37.9°F) and a boiling point of 356.7°C (674.1°F), mercury has one of the widest ranges of its liquid state of any metal.

Mercury occurs in deposits throughout the world mostly as cinnabar (mercuric sulfide, HgS), which is the source of the red pigment vermilion, and is mostly obtained by reduction from cinnabar. Cinnabar is highly toxic by ingestion or inhalation of the dust, and mercury poisoning can also result from exposure to soluble forms (such as mercuric chloride, HgCl_2 , or methylmercury, CH_3HgCH_3), inhalation of mercury vapor, or eating fish contaminated with mercury.

Mercury has been identified as a dangerous environmental contaminant, largely by reason of the process of concentration in the food chain. Thus, the presence of mercury in coal is an extremely sensitive issue. The possible emission of mercury that may be found in coal is an environmental concern.

Mercury is a common trace contaminant in natural gas, natural gas liquids, and other hydrocarbon sources. Mercury can be present in hydrocarbon derivatives in the form of ionic mercury species, organic mercury compounds, and metallic mercury. Mercury problems can be related to its toxicity (exposure during maintenance and inspection) and to the properties of the liquid metal regarding corrosion by embrittlement of sensitive alloys.

The solubility of mercury in hydrocarbon derivatives depends on the species involved, temperature, and the type of hydrocarbon derivatives. In addition, mercury can be converted from one species to another during various refinery processes. Mercury can be removed from hydrocarbon feedstocks or products by a number of processes, but the mercury species must be known for the most effective method to be employed.

Regenerative mercury removal adsorbents not only dry these streams but also remove mercury to less than 0.01 micrograms per normal cubic meter. Since the sorption sites for mercury removal are separate from and additive to the dehydration sites, mercury removal is accomplished by replacing a portion of the dehydration grade molecular sieve with specific adsorbents. The dryer bed size does not have to be increased to remove both water and mercury.

Molecular sieve products that contain silver on the outside surface of the molecular sieve pellet or bead. Mercury from the process fluid (either gas or liquid) amalgamates with the silver, and a mercury-free dry process fluid is obtained. Adding a layer of one of the adsorbents to an existing dryer results in the removal of both the design water

load and the mercury without requiring a larger dryer. Mercury and water are both regenerated from the adsorbents using conventional gas dryer techniques.

See also: Gas Cleaning.

Meson

A meson is a subatomic particle composed of an equal number of quarks and antiquarks (usually one of each) that are bound together by strong interactions. A meson has a meaningful physical size, a diameter on the order of one femtometer (1×10^{-15} meter), which is approximately 1.2 times the size of a proton or neutron. All mesons are unstable, with the longest-lived lasting for only a few hundredths of a microsecond. Charged mesons decay (sometimes through mediating particles) to form electrons and neutrinos. An uncharged meson may decay to a photon.

See also: Electron, Muon, Neutrino, Photon.

Mesosphere

The mesosphere forms the top-most layer of the homosphere. The absence of high levels of radiation-absorbing species in the mesosphere (the third layer of the atmosphere, directly above the stratosphere and directly below the thermosphere) immediately above the stratosphere results in a further temperature decrease to approximately -92°C (-134°F) at an altitude ca. 53 miles (ca. 85 km). The upper regions of the mesosphere define a region (the exosphere) from which molecules and ions can completely escape the atmosphere. Extending to the far outer reaches of the atmosphere is the thermosphere, in which the highly rarified gas reaches temperatures as high as $1,200^{\circ}\text{C}$ ($2,200^{\circ}\text{F}$) by the absorption of very energetic radiation of wavelengths less than approximately 500 nanometers (nm) by gas species in this region.

Air temperatures in the mesosphere decrease upward to a minimum of -90°C at the mesopause, the boundary with the overlying thermosphere. The upper mesosphere is the second temperature minima in the atmosphere.

Metal Oxide Processes

These processes scavenge hydrogen sulfide and organic sulfur compounds (mercaptans) from gas streams through reactions with solid-based media. They are typically non-regenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most dry sorption processes are governed by the reaction of a metal oxide with hydrogen sulfide to form a metal sulfide compound. For regenerable reactions, the metal sulfide compound can then react with oxygen to produce elemental sulfur and a regenerated metal oxide. The primary metal oxides used for dry sorption processes are iron oxide and zinc oxide.

Dry sorption processes can be categorized into two subgroups: oxidation to sulfur and oxidation to oxides of sulfur. Because these processes rely on oxidation, gas constituents that cannot be oxidized under the process conditions will not be removed. This is advantageous when dealing with biogas, as only hydrogen sulfide, mercaptans, and, in some cases, carbon dioxide will be removed, with miniscule losses of methane due to adsorption. The main product of sulfur oxidation to oxides of sulfur is sulfur dioxide. Because this is a controlled exhaust gas, poses a threat to equipment due to corrosion and poisoning of fuel cell membranes, and requires additional gas processing to achieve air discharge standards, it will not be addressed as a gas processing option.

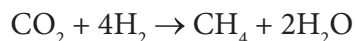
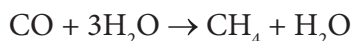
Generally, the iron oxide process is suitable only for small-to-moderate quantities of hydrogen sulfide. Approximately 90% of the hydrogen sulfide can be removed per bed, but bed clogging by elemental sulfur occurs and the bed must be discarded and the use of several beds in series is not usually economical. Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stretford process. The Ferrox process is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid.

See also: Gas Cleaning.

Methanation

Methanation is the conversion of carbon monoxide and carbon dioxide (CO_x) to methane (CH_4) through by means of hydrogenation. The process is a means of carbon oxide removal from process gases. Methanation is also a means of producing synthetic natural gas (SNG, methane).

In wet scrubbing plants, the final hydrogen purification procedure involves is by methanation in which the carbon monoxide and carbon dioxide are converted to methane:



The active agent is nickel, on an alumina carrier. The catalyst has a long life, as it operates under ideal conditions and is not exposed to poisons. The main source of deactivation is plugging from carry-over of carbon dioxide from removal solutions.

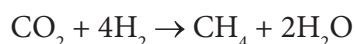
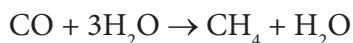
The most severe hazard arises from high levels of carbon monoxide or carbon dioxide that can result from breakdown of the carbon dioxide removal equipment or from exchanger tube leaks that quench the shift reaction. The results of breakthrough can be severe, since the methanation reaction produces a temperature rise of 70°C (125°F) per 1% of carbon monoxide or a temperature rise of 33°C (60°F) per 1% of carbon dioxide. While the normal operating temperature during methanation is approximately 315°C (600°F), it is possible to reach 700°C ($1,300^\circ\text{F}$) in cases of major breakthrough.

See also: Methanation Catalysts.

Methanation Catalysts

The current technology for upgrading biogas focuses on removing carbon dioxide from the biogas. However, the biogas could potentially be used directly as feed gas for the Sabatier reaction, thereby removing the cost associated with carbon dioxide removal and increasing the methane yield and carbon utilization from biological sources. Carbon dioxide methanation requires a catalyst to be active at relatively low temperatures and selective toward methane. Nickel-based catalysts are most widely investigated, and commercial catalysts are typically nickel on alumina support. Focus on catalyst development for carbon dioxide methanation is predominantly related to support modification, promoter addition, as well as utilizing new class of materials such as hydrotalcite-derived catalysts.

In wet scrubbing plants, the final hydrogen purification procedure involves methanation in which the carbon monoxide and carbon dioxide are converted to methane. The active agent is nickel, on an alumina carrier.



The catalyst has a long life, as it operates under ideal conditions and is not exposed to poisons. The main source of deactivation is plugging from carry-over of carbon dioxide from removal solutions.

The most severe hazard arises from high levels of carbon monoxide or carbon dioxide that can result from breakdown of the carbon dioxide removal equipment or from exchanger tube leaks which quench the shift reaction. The results of breakthrough can be severe, since the methanation reaction produces a temperature rise of 70°C (125°F) per 1% of carbon monoxide or a temperature rise of 33°C (60°F) per 1% of carbon dioxide. While the normal operating temperature during methanation is approximately 315°C (600°F), it is possible to reach 700°C ($1,300^\circ\text{F}$) in cases of major breakthrough.

See also: Methanation.

Methane

Methane (CH₄) is the simplest alkane. It is gaseous and the principal component of natural gas. Combustion of methane produces carbon dioxide and water. At room temperature and pressure, methane is a colorless, odorless gas. The smell characteristic of natural gas as used in homes is an artificial safety measure caused by the addition of an odorant, often methanethiol (CH₃SH) or ethanethiol (C₂H₅SH). Methane has a boiling point of -161°C (-258°F) at a pressure of one atmosphere (Table M-1). As a gas, methane is flammable only over a range of concentrations (5 to 15% v/v) in air. Liquid methane does not burn unless subjected to high pressure (normally 60 to 70 psi, 4 to 5 atmospheres).

Table M-1 Boiling point and density of methane relative to air and water.

• Boiling Point (760 mm Hg): -161.5°C (-258.7°F)
• Gas Specific Gravity: 0.55 to 0.64 (air = 1.00)
• Specific Gravity of Liquefied Natural Gas: 0.42 to 0.46 (water = 1.00)
• Gas Density (varies slightly): 0.0438 lb/scf

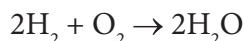
The relative abundance of methane makes it an attractive fuel, and, in its natural gas form, it is generally transported in bulk by pipeline or LNG carriers. However, methane is a relatively potent greenhouse gas and in the atmosphere is eventually oxidized, producing carbon dioxide and water.

Large amounts of methane are produced anaerobically by methanogenesis. Other sources include mud volcanoes, which are connected with deep geological faults, landfill, and livestock (primarily ruminants) from enteric fermentation.

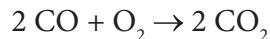
In the combustion of methane, several steps are involved: methane forms formaldehyde (HCHO) to produce a formyl radical (HCO), which then forms carbon monoxide (CO):



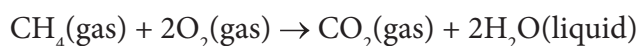
Following oxidative pyrolysis, the hydrogen oxidizes, forming water:



Finally, the carbon monoxide oxidizes, forming carbon dioxide:



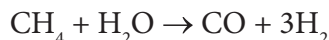
Thus:



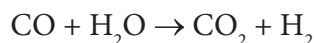
Methane is important for electrical generation by combustion as a fuel in a gas turbine or steam boiler. In many cities, methane (natural gas) is piped into homes for domestic heating and cooking purposes.

Methane is used in industrial chemical processes and may be transported as a refrigerated liquid (liquefied natural gas, or LNG). While leaks from a refrigerated liquid container are initially heavier than air due to the increased density of the cold gas, the gas at ambient temperature is less dense (lighter) than air.

In the chemical industry, methane is the feedstock of choice for the production of hydrogen, methanol, acetic acid, and acetic anhydride. When used to produce any of these chemicals, methane is first converted to synthesis gas, a mixture of carbon monoxide and hydrogen, by steam reforming. In this process, methane and steam react on a nickel catalyst at high temperatures (700–1,100 °C).



The ratio of carbon monoxide to hydrogen in synthesis gas can then be adjusted via the water gas shift reaction to the appropriate value for the intended purpose.



Less significant methane-derived chemicals include acetylene, prepared by passing methane through an electric arc, and the chloromethanes (chloromethane, dichloromethane, chloroform, and carbon tetrachloride), which are produced by reacting methane with chlorine gas. However, the use of these chemicals is declining. Acetylene is replaced by less costly substitutes, and the use of chloromethanes is diminishing due to health and environmental concerns.

See also: Acetogenesis, Acidogenesis, Alkanes, Landfill Gas, Natural Gas.

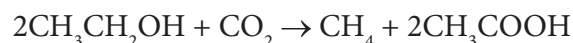
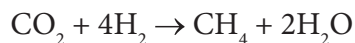
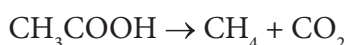
Methane Number

The methane number is a measure of the resistance of natural gas to detonation when it is burned as a motor fuel in an engine. Pure methane is assigned a methane number of 100, and pure hydrogen is assigned a methane number of zero. A natural gas having a methane number of 80 for example, would have the detonation properties of a mixture consisting of 80 vol% methane and 20 vol% hydrogen. The methane number concept is similar to the octane number for gasoline. Unlike gasoline however, there is not yet a universal standard for testing natural gas methane number as there is in the motor test for gasoline. Also, there is no universally accepted method for calculating the methane number based on the composition of natural gas.

The definition of the methane number is simple if the gas consists only of the two components methane and hydrogen. But for hydrocarbon gas mixtures consisting not only of methane but also of ethane and heavier, the definition is much more difficult and is the subject of much debate and controversy. There are various proposed methods of calculating the methane number based on gas composition. Some are methods proposed by standards associations in Europe, and some are proprietary methods proposed by engine manufacturers.

Methanogenesis

Methanogenesis is the terminal phase of anaerobic digestion in which methanogens use the intermediate products of the preceding phases and convert them to them into methane, carbon dioxide, and water. These components make up the majority of the biogas emitted from the system.



Two different groups of bacteria are responsible for the methane production. One group degrades acetic acid to methane, and the other produces methane from carbon dioxide and hydrogen. Under stable conditions, the majority (approximately 70% v/v) of the methane production comes from the degradation of acetic acid, while the remaining methane production (approximately 30% v/v) comes from carbon dioxide and hydrogen. The two processes are balanced, and inhibition of one will also lead to inhibition of the other. The methanogens have the slowest growth rate of the bacteria involved in the process; they also become the limiting factor for how quickly the process can proceed and how much material can be digested.

Methanogenesis is sensitive to both high pH (alkaline) and low pH (acidic) and occurs between pH 6.5 and pH 8, in near neutral conditions. The remaining, indigestible material the microbes cannot use, and any dead bacterial remains constitute the digestate.

Methane-producing bacteria decompose compounds with a low molecular weight. For example, they utilize hydrogen, carbon dioxide, and acetic acid to form methane and carbon dioxide. Under natural conditions, methane-producing microorganisms occur to the extent that anaerobic conditions are provided, e.g., under water (for example in marine sediments), in ruminant stomachs and in marshes. They are obligatory anaerobic and sensitive to environmental changes. In contrast to the acidogenic and acetogenic bacteria, the methanogenic bacteria belong to the archaeobacter genus, i.e., to a group of bacteria with a very heterogeneous morphology and a number of common biochemical and molecular-biological properties that distinguish them from all other bacterial general. The main difference lies in the makeup of the bacteria's cell walls.

In the overall process, the acid-producing bacteria and the methane-producing bacteria act in a symbiotic way. On the one hand, acid-producing bacteria create an atmosphere with ideal parameters for methane-producing bacteria (anaerobic conditions, compounds with a low-molecular-weight feedstock). On the other hand, methane-producing microorganisms use the intermediates of the acid-producing bacteria. Without removal (consumption) of these intermediate products from the system by the methane-producing microorganisms, toxic conditions for the acid-producing microorganisms would develop leading to an inhibition effect and a loss of process efficiency.

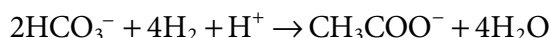
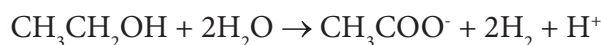
Essentially, the four phases of anaerobic degradation take place simultaneously in a single-phase process. However, as the bacteria involved in the various phases of degradation have different requirements in terms of habitat (regarding pH value and temperature, for example), a compromise has to be found in the process technology. Since the methanogenic microorganisms are the weakest link in the four phases because of the low rate of growth of the methanogens and they are the most sensitive to respond to disturbances, the digester conditions have to be adapted to the requirements of the methane-forming bacteria. However, any attempt to physically separate hydrolysis and acidogenesis from methanogenesis by implementing two distinct process phases (two-phase process management) will succeed to only a limited extent because, despite the low pH value in the hydrolysis phase ($\text{pH} < 6.5$), some methane will still be formed. The resulting hydrolysis gas therefore also contains methane in addition to carbon dioxide and hydrogen. In multi-phase processes, different environments can become established in the individual digester phases depending on the design of the biogas plant and its operating regime, as well as on the nature and concentration of the fresh mass used as substrate. In turn, the ambient conditions affect the composition and activity of the microbial biocoenosis and thus have a direct influence on the resulting metabolic products.

As a recap, Phase 1 of the process is the hydrolysis reaction in which high-molecular-weight naturally-occurring compounds (cellulose, hemicellulose, and lignin) are converted to lower-molecular-weight products. Typically sugars and oxygenated aromatic derivatives. During acidogenesis, soluble monomers are converted into small organic compounds, such as short chain (volatile) acids (propionic, formic, lactic, butyric, succinic acids), ketones (glycerol, acetone), and alcohols (ethanol, methanol). Generally, the chemistry of Phase 2 (acidogenesis) and Phase 3 (acetogenesis) can be represented by a series of simple equations:

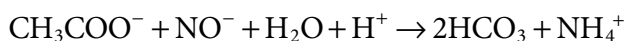
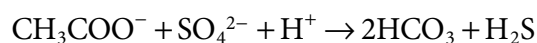
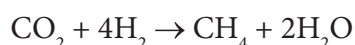
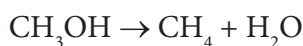
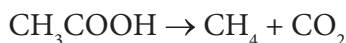
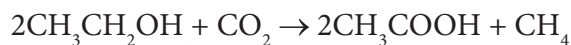
Acidogenesis:



Acetogenesis:



Phase IV is the phase of methane formation (methanogenesis) in which the concentrations of the intermediate acids are small in proportion to their production and degradation rates, and they are quickly transformed to methanogenic substrates, including acetate, methanol, and formate. Thus, the last phase of anaerobic digestion is the methanogenesis phase. Several reactions take place using the intermediate products from the other phases, with the main product being methane. The reactions are commonly represented as:



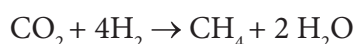
Several bacterial contribute to methanogenesis, including: Methanobacterium, methanobacillus, methanococcus, and methanosarcina.

Any kind of organic matter can be fed to an anaerobic digester, including manure and litter, food wastes, green wastes, plant biomass, and wastewater sludge. The materials that compose these feedstocks include polysaccharides, proteins, and fats/oils. Some of the organic materials degrade at a slow rate; hydrolysis of cellulose and hemicellulose is rate limiting (Amani et al., 2010). There are some organic materials that do not biodegrade: lignin, peptidoglycan (a polymer consisting of sugar derivatives and amino acid derivatives that forms a mesh-like layer outside the plasma membrane of most bacteria, forming the cell wall), and membrane-associated proteins. The organic residues contain water and biomass composed of volatile solids and fixed solids (minerals or ash after combustion), and it is the volatile solids that can be non-biodegradable and biodegradable. However, unlike the chemistry of the anaerobic digester, the organic waste in the landfill is not available for separate pretreatment unless there is a form of pretreatment before the material is discharged into the landfill.

See also: Acetogenesis, Acidogenesis, Acidogenic Digestate, Hydrolysis – Anaerobic Digestion.

Methanogens

Methanogens are methane-producing microorganisms that are usually coccoid (spherical) or bacilli (rod shaped). They are anaerobic organisms and cannot function under aerobic conditions, being sensitive to the presence of oxygen even at trace levels. Some methanogens (hydrogenophobic organisms) use carbon dioxide (CO_2) as a source of carbon, and hydrogen as a reducing agent:



Methanogens typically thrive in environments in which all electron acceptors other than carbon dioxide (such as oxygen, nitrate, trivalent iron, and sulfate) have been depleted. Methanogens are key agents of remineralization of organic carbon in sediments on continental margins and other aquatic sediments with high rates of sedimentation and high sediment organic matter. Under the correct conditions of pressure and temperature, biogenic methane can accumulate in massive deposits of methane clathrates (methane hydrates), which account for a significant fraction of organic carbon in continental margin sediments and represent a key reservoir of a potent greenhouse gas.

Closely related to the methanogens are the anaerobic methane oxidizers, which utilize methane as a substrate in conjunction with the reduction of sulfate and nitrate. Most methanogens are autotrophic producers, but those that oxidize acetate (CH_3COO^-) are classed as chemotrophic producers.

Methanol

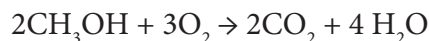
Methanol (CH_3OH ; methyl alcohol; wood alcohol, wood naphtha, wood spirits) is a colorless, volatile, inflammable, and poisonous alcohol traditionally formed by destructive distillation of wood or, more recently, as a result of synthetic distillation in chemical plants. It is the simplest alcohol, and is a low-boiling, volatile, colorless, flammable, poisonous liquid with a distinctive odor that is somewhat milder and sweeter than ethanol (ethyl alcohol). At room temperature, methanol is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethyl alcohol. It is also used for producing biodiesel via transesterification reaction.

Methanol is a colorless, odorless, and nearly tasteless alcohol and is also produced from crops and is also used as a fuel. Methanol, like ethanol, burns more completely but releases as much or more carbon dioxide than its gasoline counterpart. The balance is often seen as the various bi-processes that draw carbon dioxide from the atmosphere so there is no net modern release, as there is for fossil fuels.

Pyrolysis (heating wood in the absence of air) to a temperature above 270°C (520°F) in a retort causes thermal cracking or breakdown of the wood and allows much of the wood to be recovered as charcoal. The watery condensate leaving the retort contained methanol, among other compounds.

Methods proposed for the production of methanol from biomass involve the conversion of the biomass to synthesis gas, after which the processing steps are similar to those developed for methanol from natural gas. However, before biomass can be gasified, it must be pre-treated to meet the processing constraints of the gasifier. This typically involves size reduction, and drying to keep moisture contents below specific levels. Thereafter, biomass gasification involves heating biomass in the presence of low levels of oxygen (i.e., less than required for complete combustion to carbon dioxide and water). Above certain temperatures, the biomass will break down into a gas stream and a solid residue. The composition of the gas stream is influenced by the operating conditions for the gasifier, with some gasification processes more suited than others to producing a gas for methanol production. In particular, simple gasification with air creates a synthesis gas stream that is diluted with large quantities of nitrogen. This nitrogen is detrimental to subsequent processing to methanol, and so techniques using indirect gasification or an oxygen feed are preferred.

Methanol burns in air forming carbon dioxide and water:

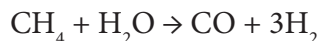


A methanol flame is almost colorless, causing an additional safety hazard around open methanol flames.

Because of its poisonous properties, methanol is frequently used as a denaturant additive for ethanol manufactured for industrial uses – this addition of a poison economically exempts industrial ethanol from the rather significant liquor taxes that would otherwise be levied as it is the essence of all potable alcoholic beverages. Methanol is often called wood alcohol because it was once produced chiefly as a by-product of the destructive distillation of wood. It is now produced synthetically by a multi-step process: natural gas and steam are reformed in a furnace to produce hydrogen and carbon monoxide; then, hydrogen and carbon monoxide gases react under pressure in the presence of a catalyst.

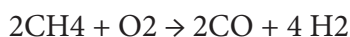
The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability and low cost. Problems occurred early in the development of gasoline-methanol blends. As a result of its low price, some gasoline marketers over-blended. Others used improper blending and handling techniques.

Synthesis gas is most commonly produced from the methane component in natural gas rather than from coal. Three processes are commercially practiced. At moderate pressures (of 150 to 300 psi) and high temperatures (around 850°C), methane reacts with steam on a nickel catalyst to produce synthesis gas:

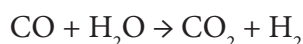


This reaction, commonly called steam-methane reforming, is endothermic, and the heat transfer limitations place limits on the size of and pressure in the catalytic reactors used.

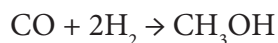
Methane can also undergo partial oxidation with molecular oxygen to produce synthesis gas:



This reaction is exothermic, and the heat given off can be used in-situ to drive the steam-methane reforming reaction. When the two processes are combined, it is referred to as autothermal reforming. The ratio of carbon dioxide to hydrogen can be adjusted to some extent by the water-gas shift reaction:



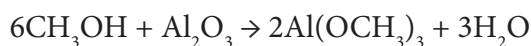
This reaction provides the appropriate stoichiometry for methanol synthesis. The carbon monoxide and hydrogen then react on a second catalyst to produce methanol. The most widely used catalyst is a mixture of copper, zinc oxide, and alumina (at 50 to 100 atmospheres and 250°C, 480°F) which catalyzes the production of methanol from carbon monoxide and hydrogen with high selectivity:



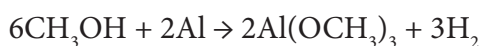
The production of synthesis gas from methane produces 3 moles of hydrogen for every mole of carbon monoxide, while the methanol synthesis consumes only 2 moles of hydrogen for every mole of carbon monoxide. One way of dealing with the excess hydrogen is to inject carbon dioxide into the methanol synthesis reactor, where it, too, reacts to form methanol:



The largest use of methanol by far, is in making other chemicals. Approximately 40% of methanol is converted to formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles. One of the drawbacks of methanol as a fuel is its corrosivity to some metals, including aluminum. Methanol, although a weak acid, attacks the oxide coating that normally protects the aluminum from corrosion:



The resulting methoxide salts are soluble in methanol, resulting in clean aluminum surface, which is readily oxidized by some dissolved oxygen. Also, the methanol can act as an oxidizer:



This reciprocal process effectively fuels corrosion until either the metal is eaten away or the concentration of methanol is negligible.

When produced from wood or other organic materials, the resulting organic methanol (bioalcohol) has been suggested as renewable alternative to petroleum-based hydrocarbon derivatives. However, one cannot use pure methanol in modern petroleum cars without modification, due to potential damage to metal piping and rubber seals.

Methanol is a traditional denaturant for ethanol, thus giving the term methylated spirit. Methanol is also used as a solvent, and as antifreeze in pipelines and windshield washer fluid. In some wastewater treatment plants, a small amount of methanol is added to wastewater to provide a food source of carbon for the denitrifying bacteria, which convert nitrates to nitrogen.

Methanol is probably one of the most versatile solvents in the natural gas processing industry. Historically, methanol was the first commercial organic physical solvent and has been used for hydrate inhibition, dehydration, gas sweetening, and liquids recovery. Most of these applications involve low temperature where the physical properties of methanol are advantageous compared with other solvents that exhibit high viscosity problems or even solids formation. Operation at low temperatures tends to suppress the most significant disadvantage of using methanol, i.e., high solvent loss.

Methanol has favorable physical properties relative to other solvents except for vapor pressure. The benefits of the low viscosity of methanol at low temperature are manifested in the pressure drop improvement in the cold box of injection facilities and improved heat transfer. Methanol has a much lower surface tension relative to the other solvents. High surface tension tends to promote foaming problems in contactors. Methanol processes are probably not susceptible to foaming. However, the primary drawback of methanol is the high vapor pressure that is several times

greater than that of the glycols or amines. To minimize methanol losses and enhance water and acid gas absorption, the absorber or separator temperatures are usually less than -29°C (-20°F).

The high vapor pressure of methanol may initially appear to be a significant drawback because of high solvent losses. However, the high vapor pressure also has significant advantages. Although often not considered, lack of thorough mixing of the gas and solvent can pose significant problems. Because of the high vapor pressure, methanol is completely mixed in the gas stream before the cold box. Glycols, because they do not completely vaporize, may require special nozzles and nozzle placement in the cold box to prevent freeze-up. Solvent carry-over to other downstream processes may also represent a significant problem. Since methanol is more volatile than glycols, amines, and other physical solvents including lean oil, methanol is usually rejected in the regeneration step of these downstream processes. The stripper concentrates the methanol in the overhead condenser where it can be removed and further purified. Unfortunately, if glycols are carried over to amine units, the glycol becomes concentrated in the solution and potentially starts to degrade and possibly dilute the amine solution.

Methanol has been extensively used as a hydrate inhibitor, but predicting the behavior of methanol is complicated and, in fact, the thermodynamic properties and phase equilibrium of mixtures of methanol, water, and hydrocarbon derivatives are notoriously difficult to predict. Methanol shows both polar and non-polar characteristics. Consequently, these characteristics give methanol the unique ability to be used in an extensive range of applications.

See also: Gasification, Gasification of Biomass, Methanol – Production, Synthesis Gas.

Methanol – Production

Methanol and other chemicals were routinely extracted from wood in the 19th and early 20th centuries. However, the original route for methanol recovery from biomass was quite different to current routes. Methanol was originally recovered from wood as a by-product of charcoal manufacture, and was often called “wood alcohol.” Pyrolysis (heating wood in the absence of air) to above 270°C in a retort causes thermal cracking or breakdown of the wood and allows much of the wood to be recovered as charcoal. In 1923, commercial production of methanol from synthesis gas by a catalytic process was commenced. Currently, almost all of the methanol used worldwide comes from the processing of natural gas.

Methanol is manufactured from natural gas by a steam reforming process. Methane of natural gas is first mixed with steam at 3/1 ratio. It is then reformed to carbon oxides and hydrogen under nickel catalyst at 1000°C (1830°F) and 20 atmospheres. Carbon oxides and hydrogen reacts exothermically at approximately 70 atmospheres pressure in the gas phase to form mainly methanol and water mixture. These reactions take place in the presence of Cu, Al, and Zn-based catalyst. Crude methanol is cooled and condensed and fed through a distillation process to achieve a product purity of 99.9 mole%. As an alternative, partial oxidation or oxygen aided processes are also used.

As with any fuel, methanol production economics are highly dependent on the feedstock selection and feedstock prices. Methanol can be manufactured from any hydrocarbon source such as: naphtha, oil, coal, wood, bio-mass, and LPG. The naphtha – a fraction from crude oil distillation – is used as a raw material in many older facilities for the manufacture of methanol.

In general, methanol production from natural gas feed consists of three steps which are (i) synthesis gas (syngas) generation – in the case of natural gas feed, synthesis gas production consists of converting methane (CH_4) into carbon monoxide (CO) and hydrogen (H_2) via steam reforming, (ii) synthesis gas upgrading – primarily removal of CO_2 , plus any contaminants such as sulfur, and (iii) methanol synthesis and purification – reacting the carbon monoxide, hydrogen, and steam over a catalyst in the presence of a small amount of CO_2 and at elevated temperature and pressure. The methanol synthesis is an equilibrium reaction, and excess reactants must be recycled to optimize yields.

Modern methods proposed for the production of methanol from biomass involve the conversion of the biomass to a suitable synthesis gas, after which the processing steps are similar to those developed for methanol from natural gas. However, the gasification techniques proposed are still at a relatively early stage of development using biomass feed and the methods are based on similar techniques used widely already with natural gas as feed.

Before biomass can be gasified, it must be pre-treated to meet the processing constraints of the gasifier. This typically involves size reduction, and drying to keep moisture contents below specific levels. Thereafter, biomass gasification involves heating biomass in the presence of low levels of oxygen (i.e., less than required for complete combustion to carbon dioxide and water). Above certain temperatures, the biomass will break down into a gas stream and a solid residue.

The composition of the gas stream is influenced by the operating conditions for the gasifier, with some gasification processes more suited than others to producing a gas for methanol production. In particular, simple gasification with air creates a synthesis gas stream that is diluted with large quantities of nitrogen. This nitrogen is detrimental to subsequent processing to methanol, and so techniques using indirect gasification or an oxygen feed are preferred. For large-scale gasification, pressurized systems are considered to be more economic than atmospheric systems.

Once the economic optimum synthesis gas is available, the methanol synthesis takes place. This typically uses a copper-zinc catalyst at temperatures of 200 to 280°C (390 to 540°F) and pressures of 50 to 100 atmospheres.

The crude methanol from the synthesis loop contains water produced during synthesis as well as other minor by-products. Purification is achieved in multistage distillation, with the complexity of distillation dictated by the final methanol purity required.

See also: Gasification, Gasification of Biomass, Methanol, Synthesis Gas.

Methanol – Properties

Methanol (methyl alcohol, carbinol, methyl hydroxide, methylol, monohydroxy methane, wood alcohol, colonial spirit, hydroxy methane, wood naphtha) has properties that are consistent with the low molecular weight but also consistent with the ability of the molecule to form intermolecular hydrogen bonds (Table M-2).

Table M-2 Selected properties of methanol compared to ethanol.

Property	Methanol	Ethanol
	CH₃OH	C₂H₅OH
Molecular weight	32	46
Specific gravity	0.789 (298 K)	0.788 (298 K)
Vapor density relative to air	1.10	1.59
Liquid density (g cm ⁻³ at 25°C)	0.79	0.79
Boiling point (°C)	65	78
Melting point (°C)	-98	-144
Vapor pressure @ 100°C (psia)	4.6	2.5
Heat of evaporation (Btu/lb)	472	410
Heating value (kBtu per gallon)		
Lower	58	74
Upper	65	85
Viscosity (cp)	0.54	1.20
Flash point (K)	284	287
Flammability/explosion limits		
- (%) Lower (LFL)	6.7	3.3
- (%) Upper (UFL)	36	19
Auto ignition temperature (K)	733	636
Solubility in water (%)	Miscible(100%)	Miscible (100%)
Azeotrope with water	None	95% v/v EtOH

The density of methanol at room temperature, at 25°C, is 0.7918 g/cm³. The heat of formation for methanol as gas ($\Delta H^\circ_{f,\text{gas}}$) is -201.1 ± 0.2 kJ/mol, whereas that for the liquid methanol ($\Delta H^\circ_{f,\text{liquid}}$) is -239.5 ± 0.2 kJ/mol. The constant-pressure heat capacity of methanol as gas ($C_{p,\text{gas}}$) at room temperature is 44 J/°K-mol, while that for liquid methanol is 80 ± 1 J/°K-mol. The Henry's law constant (K_H) for solubility of methanol in water at 298.15 °K is 210 ± 10 mol/kg-bar.

The critical temperature and pressure of methanol are 513 ± 1.2 °K and 81 ± 1.0 bars, respectively, while the normal boiling and melting temperatures are 337.8 ± 0.3 °K and 176.0 ± 1.0 °K, respectively. The triple point of methanol is 175.5 ± 0.5 °K. The flash point of methanol is 11°C. The enthalpy of vaporization of methanol at room temperature ($\Delta H^\circ_{\text{vap}}$) is 37.83 kJ/mol². Methanol can be used as a supercritical solvent or co-solvent for a variety of modern processes. The hydroxyl group in its molecular structure renders unique properties that are normally not attained from carbon dioxide. Its critical point is harsher than carbon dioxide, but milder than water.

The acidity of methanol is $\text{pK}_a = \sim 15.5$ and viscosity is 0.54 cP at 20°C (68°F). Due to its low freezing point, methanol has been popularly used as a cold-weather windshield washer fluid. A concentration of 30% by wt. can provide anti-freezing protection of -20°C (-4°F). Due to the hydroxyl group in methanol, it has a strong tendency of hydrogen bonding. A hydrogen bond is not a true bond, but a particularly strong form of dipole-dipole interaction. The hydroxyl (O-H) bonds are strongly polarized, thus leaving the hydrogen atom with a partially positive charge, which is electrophilic hydrogen. This hydrogen has a strong affinity for nonbonding electrons, and as such, it forms intermolecular attachments with the nonbonding electrons on oxygen atom. Comparing the two isomers between ethanol (C₂H₅OH) and dimethyl ether (CH₃OCH₃), both of which have a formulation of C₂H₆O, one can immediately notice that ethanol has much higher boiling point (78°C, 172°F) than that of dimethyl ether (-25°C, 13°F). This striking difference of approximately 100°C (180°F) in the respective boiling points is due to the fact that ethanol has hydroxyl (O-H) hydrogen which is extensively hydrogen-bonded, whereas dimethyl ether has no hydroxyl hydrogen, thus without the benefit of hydrogen bonding.

Methanol also reacts easily with carboxylic acids to produce esters from which water is a by-product of condensation type of reaction. The presence of methyl group in the formula provides chemical affinity toward hydrocarbon derivatives, and as such, methanol shows excellent solubility toward a variety of organic materials, while the presence of hydroxyl group renders excellent water miscibility. The dual nature of the solubility makes methanol as a good candidate for oxygenate fuel as well as water remover from gasoline. As a water remover in a gasoline fuel system, presence of methanol in the formulation creates a miscible ternary mixture (gasoline-methanol-water) instead of an immiscible binary mixture (gasoline-water).

Methanol has an octane rating of 105 (Research Octane Number, RON) and can be used as an octane enhancer. Since high performance with a higher compression ratio requires a higher octane rating than its regular counterparts, methanol is used as a racing fuel. Due to the high oxygen content (50% by mass) in the methanol molecular structure, it appears to be an excellent oxygenate fuel. However, it should be noted that its blending vapor pressure increase is substantially higher than other competing oxygenate blends such as MTBE (methyl-t-butyl ether) and ethanol, thus making it unpopular as a gasoline blending fuel. The vapor pressure increase due to gasoline blending is typically measured by Reid vapor pressure. The high vapor pressure of blended gasoline can increase the chance for evaporative emission of the fuel as well as the risk of having "vapor lock" in the fuel line. Furthermore, the toxicity of methanol, if inhaled or internally taken, is far more serious than that of ethanol. Evaporative fuel emission is particularly of concern to environmental air quality during summer months, when the emitted hydrocarbon is linked with the environmental health problem of "high ozone level in the air."

The common method for measuring the vapor pressure of crude oil products is the Reid vapor pressure test, or RVP test. There are basically two methods approved also by ASTM, i.e., Reid method (ASTM D323) and dry method (ASTM D4953). The Reid method covers experimental measurements of vapor pressure of gasoline, volatile crude oil, and other volatile crude oil products that include crude oil crude, gasoline, MTBE-blended gasoline, aviation fuel, and other crude oil products. There are four procedures provided by this method, depending upon the types and vapor pressure ranges of the tested fuel. However, this method is not applicable to liquefied crude oil gas (LPG) and oxygenated gasoline except MTBE-blended gasoline.

For the determination of the vapor pressure of liquefied crude oil gases (LPG), ASTM D1267 is the recommended test method whereas determination of the vapor pressure of gasoline-oxygenate blends refers to ASTM D4953. The

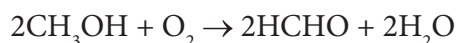
latter method is referred to as the dry method, which is applicable to most oxygenated gasolines, except MTBE-blended gasoline, with a vapor pressure range from 5 to 15 psi. There are thermodynamic algorithms developed for estimation of RVP without performing actual measurement.

See also: Methanol, Methanol – Production.

Methanol – Reactions

Pure methanol is an important material in chemical synthesis. Its derivatives are used in great quantities for building up a vast number of compounds, among them many important synthetic dyestuffs, resins, drugs, and perfumes. Large quantities are converted to dimethyl aniline for dyestuffs and to formaldehyde for synthetic resins. It is also used in automotive antifreezes, in rocket fuels, and as a general solvent. Methanol is also a high-octane, clean-burning fuel that is a potentially important substitute for gasoline in automotive vehicles.

Methanol is used to produce formaldehyde via an oxidation reaction in which approximately 40% of methanol is converted to formaldehyde (HCHO), and from there into products as diverse as thermosetting polymers, plywood, paints, explosives, and permanent press textiles.



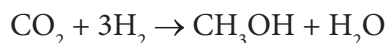
Methanol is also used for making a variety of ethers including MTBE (methyl-t-butyl ether), ETBE (ethyl-t-butyl ether), TAME (t-amyl-methyl ether), DME (dimethyl ether), etc. The first three are normally synthesized by catalytic distillation (CD), whereas the fourth is produced by catalytic dehydration. As the name implies, catalytic distillation is a hybrid process between a well-established unit operation of distillation and a catalytic chemical reaction. Methanol also readily reacts with carboxylic acids to produce methyl esters of these acids. These esters, in particular fatty acid esters, are quite important as ingredients for biodiesel, fuel additives, fuel system cleaners, octane enhancers, biodiesel formulations, etc.

Dimethyl ether (DME) is gaining extra significance as a renewable fuel. Dimethyl ether has always been considered a major derivative of methanol, and its synthesis is based on the following stoichiometric equation:



Methanol serves as a direct reactant or as an intermediate in the synthesis of dimethyl ether, depending upon the reaction routes.

The first process route is based on conventional dehydration of methanol over a dehydration catalyst, where methanol is a direct reactant and dimethyl ether and water are recovered as products. This process is carried out as a stand-alone type of process. In recent years, however, the second process option where methanol is an intermediate in the conversion of synthesis gas to dimethyl ether, i.e., single-stage synthesis of dimethyl ether from synthesis gas, has attracted a great deal of attention.



The process benefits have been two-fold, one being that the direct synthesis of dimethyl ether from synthesis gas can overcome the equilibrium limitation imposed by methanol synthesis reaction and the other being the reaction of converting methanol into dimethyl ether is an important precursor step for methanol-to-hydrocarbon conversion processes represented by the methanol-to-olefin process (MTO process) and the methanol-to-gasoline process (MTG process).

Even if dimethyl ether itself is considered a final product, the direct route via single-stage synthesis is far more advantageous from the standpoints of both production cost and process efficiency. The single-stage synthesis of dimethyl ether exploits the equilibrium-unlimited dehydration of methanol to dimethyl ether to its fullest extent by alleviating the equilibrium-limited nature of the methanol synthesis reaction. This is accomplished via a dual catalytic system in which in-situ produced methanol is selectively removed from the reaction equilibrium by converting the product methanol to dimethyl ether. In this process, methanol concentration in the reactor is being kept low, thus keeping the methanol synthesis portion of the overall conversion process far from its chemical equilibrium. Catalyst 1, such as $\text{Cu/ZnO/Al}_2\text{O}_3$, does the first reaction of methanol synthesis, whereas Catalyst 2, such as $\gamma\text{-Al}_2\text{O}_3$, catalyzes dehydration of methanol. Both reactions are carried out in the very same reactor, and therefore, such reaction system is called a dual catalytic system. Obviously, as an advantage, a higher once-through conversion of synthesis gas to dimethyl ether can be attained.

Direct methanol fuel cells (DMFC) are unique in their low temperature, atmospheric pressure operation, allowing them to be miniaturized to an unprecedented degree. This direct methanol fuel cell technology combined with the relatively easy and safe storage and handling of methanol may open the possibility of fuel cell-powered consumer electronics.

See also: Methanol, Methanol – Production.

Methanol-Based Processes

Methanol has favorable physical properties relative to other solvents except for vapor pressure. The benefits of the low viscosity of methanol at low temperature are manifested in the pressure drop improvement in the cold box of injection facilities and improved heat transfer. Methanol has a much lower surface tension relative to the other solvents. High surface tension tends to promote foaming problems in contactors. Methanol processes are probably not susceptible to foaming. However, the primary drawback of methanol is the high vapor pressure that is several times greater than that of the glycols or amines. To minimize methanol losses and enhance water and acid gas absorption, the absorber or separator temperatures are usually less than -29°C (-20°F).

The high vapor pressure of methanol may initially appear to be a significant drawback because of high solvent losses. However, the high vapor pressure also has significant advantages. Although often not considered, lack of thorough mixing of the gas and solvent can pose significant problems. Because of the high vapor pressure, methanol is completely mixed in the gas stream before the cold box. Glycols, because they do not completely vaporize, may require special nozzles and nozzle placement in the cold box to prevent freeze-up. Solvent carry-over to other downstream processes may also represent a significant problem. Since methanol is more volatile than glycols, amines, and other physical solvents including lean oil, methanol is usually rejected in the regeneration step of these downstream processes. The stripper concentrates the methanol in the overhead condenser where it can be removed and further purified. Unfortunately, if glycols are carried over to amine units, the glycol becomes concentrated in the solution and potentially starts to degrade and possibly dilute the amine solution.

The use of methanol has been further exploited in the development of the Rectisol process either alone or as toluene-methanol mixtures are used to remove hydrogen sulfide and slip carbon dioxide to the overhead product more selectively. Toluene has an additional advantage insofar as carbonyl sulfide (carbonyl sulfide) is more soluble in toluene than in methanol. The Rectisol process was primarily developed to remove both carbon dioxide and hydrogen sulfide (along with other sulfur-containing species) from gas streams resulting from the partial oxidation of coal, oil, and petroleum residua. The ability of methanol to absorb these unwanted components made it the natural solvent of choice. Unfortunately, at cold temperatures, methanol also has a high affinity for hydrocarbon constituents of the gas streams. For example, propane is more soluble in methanol than is carbon dioxide. There are two versions of the Rectisol process – the two-stage and the once-through. The first step of the two-stage process is desulfurization before shift conversion; the concentrations of hydrogen sulfide and carbon dioxide are approximately 1 and 5% v/v, respectively. Regeneration of the methanol following the desulfurization of the feed gas produces high sulfur feed for sulfur recovery. The once-through process is only applicable for high pressure partial oxidation products. The once-through process is also applicable when the hydrogen sulfide to carbon dioxide content is unfavorable, in the neighborhood of 1:50.

Recently, a process using methanol has been developed in which the simultaneous capability to dehydrate, to remove acid gas, and to control hydrocarbon dew point. The IFPEXOL-1 is used for water removal and hydrocarbon dew point

control; the IFPEXOL-2 process is used for acid gas removal. The novel concept behind the IFPEXOL-1 process is to use a portion of the water-saturated inlet feed to recover the methanol from the aqueous portion of the low temperature separator. That approach has solved a major problem with methanol injection in large facilities, the methanol recovery via distillation. Beyond that simple discovery, the cold section of the process is remarkably similar to a basic methanol injection process. Modifications to the process include water washing the hydrocarbon liquid from the low temperature separator to enhance the methanol recovery. The IFPEXOL-2 process for acid gas removal is similar to an amine-type process except for the operating temperatures. The absorber operates below -20°F to minimize methanol losses, and the regenerator operates at approximately 90 psi. Cooling is required on the regenerator condenser to recover the methanol. This process usually follows the IFPEXOL-1 process, so excessive hydrocarbon absorption is not as great a problem.

Methanol-to-Gasoline Process

Methanol is produced catalytically from synthesis gas, and by-products such as ethers, formic acid esters, and higher-molecular-weight hydrocarbon derivatives are formed in side reactions and are found in the crude methanol product. Whereas for many years, methanol was produced from coal; after World War II, low-cost natural gas and low-boiling crude oil fractions replaced coal as the feedstock.

Following from this, one of the most significant developments in synthetic fuels technology since the discovery of the Fischer-Tropsch process is the Mobil methanol-to-gasoline (MTG) process (now the ExxonMobil methanol-to-gasoline process) in which methanol is efficiently transformed into hydrocarbon derivatives ranging from ethane to decane by a reaction that is catalyzed by synthetic zeolites.



Olefins and aromatic compounds are also produced, and the chemistry of the reaction is more complex than this simple equation illustrates. For accuracy and economics, chemical equations should be derived for each particular aspect of the process.

In the process (which can use a fixed bed reactor or a fluid bed reactor), the methanol feed, vaporized by heat exchange with reactor effluent gases, is converted in a first-stage reactor containing an alumina catalyst to an equilibrium mixture of methanol, dimethyl ether, and water. This is combined with recycle low-boiling gas, which serves to remove reaction heat from the highly exothermic methanol-to-gasoline reaction, and enters the reactors containing zeolite catalyst, and reaction conditions are 360 to 415°C (680 to 780°F) at a pressure of approximately 300 to 350 psi.

Because the methanol-to-gasoline process produces primarily gasoline, a variation of that process has been developed which allows for production of gasoline and distillate fuel. The combined process (methanol-to-olefins and olefins-to-gasoline-and-distillate) produces gasoline and distillate in various proportions and, if needed, can be terminated at a point to produce olefin by-products.

In the process, the conversion of methanol to hydrocarbon derivatives and water is virtually complete and essentially stoichiometric in the MTG process. The reaction is exothermic with the reaction heat managed by splitting the conversion in two parts. In the first part, methanol is converted to an equilibrium mixture of methanol, dimethyl ether, and water. In the second part, the equilibrium mixture is mixed with recycle gas and passed over a shape-selective catalyst to form hydrocarbon derivatives and water. Most of the hydrocarbon product boils in the gasoline boiling range. The low-sulfur, low-benzene gasoline product from the process is a premium-quality clean gasoline and can be blended with refinery gasoline directly or sold separately.

See also: Methanol, Methanol – Production, Methanol - Reactions, Methanol-to-Olefins Process, Synthesis Gas.

Methanol-to-Olefins Process

In the UOP methanol-to-olefins (MTO) process, methanol is converted over a zeolite catalyst to give high yields of olefins with some ethylene and low-boiling low-density saturated hydrocarbon derivatives. Generally, catalyst and process variables that increase methanol conversion decrease olefins yield. In the methanol-to-olefins process,

typical conversions exceed 99.9%. The coked catalyst is continuously withdrawn from the reactor and burned in a regenerator.

The UOP/HYDRO MTO process was jointly developed by UOP and Norsk Hydro for the selective production of ethylene and propylene from methanol. The process combines well-proven fluid catalytic cracker (FCC) and naphtha cracker technologies with a proprietary new catalyst from UOP. The catalyst used in the process is based on a silico-alumino-phosphate, SAPO-34.

The MTO process converts methanol to ethylene and propylene at nearly 80% carbon selectivity in a fluidized bed reactor. The MTO reaction is exothermic. Carbon or coke accumulates on the catalyst and must be removed to maintain catalyst activity. The coke is removed by combustion with air in a catalyst regenerator system. Other co-products include small amounts of C_1 - C_4 paraffins, hydrogen, carbon monoxide, and carbon dioxide, as well as ppm levels of heavier oxygenates that are removed to ensure that the product olefins meet polymer-grade specifications.

The methanol-to-olefins process is part of a two-step process, which converts natural gas or coal to methanol followed by the conversion of methanol to low-boiling olefins.

The methanol-to-olefins process provides an alternative to naphtha cracking for the production of ethylene and propylene, and the corresponding polyolefins (GTP – gas to polyolefins) from methanol that can be produced in large quantities from natural gas or other sources such as biomass. The process is flexible with respect to the ethylene/propylene ratio, and the increased future propene demand can be met without an excessive co-production of ethylene.

See also: Methanol, Methanol – Production, Methanol – Reactions, Methanol-to-Gasoline Process, Synthesis Gas.

Methanol-to-Olefins-to-Gasoline Process

The methanol-to-olefins-to-gasoline-and-distillate process (MOGD process, now called the EMOGAS – ExxonMobil Olefins to Gasoline Process) is advanced technology for low-boiling olefins polymerization to gasoline.

In the process, low-molecular-weight olefins produce oligomers in the gasoline boiling range using a zeolite catalyst. Other distillate products are also produced. Gasoline/distillate product ratios can vary, depending on process conditions, from 0.2 to >100.

The direct conversion of natural gas (methane) to liquid fuels involves conversion of methane to the desired liquid fuels while bypassing the synthesis gas step. Direct upgrading routes which have been extensively studied include direct partial oxidation to oxygenates, oxidative coupling to higher-molecular-weight hydrocarbon derivatives, and pyrolysis to higher-molecular-weight products.

In the process, low-boiling olefins are converted to a final gasoline and diesel product. Gasoline and diesel selectivity is greater than 95% of the low-boiling olefin feedstock, and gasoline/diesel product ratios have been produced ranging 0.12 to >100. Because of the catalyst shape selectivity, most products are methyl branched iso-olefins. In the C_5 to C_{10} range, branched iso-olefins have good octane rating. In the C_{10} to C_{20} range, after hydrogenation, iso-paraffins have good diesel fuel properties.

See also: Methanol, Methanol – Production, Methanol – Reactions, Methanol-to-Gasoline Process, Methanol-to-Olefins Process, Synthesis Gas.

Methyl Alcohol

Methyl alcohol (also known as methanol and wood alcohol) is a chemical with a methyl group linked to a hydroxyl group (CH_3OH , often abbreviated to $MeOH$). It is a low-boiling colorless, flammable liquid, and polar solvent with a distinctive odor similar to the odor of ethyl alcohol.

Methanol is used as a precursor to commodity chemicals, including formaldehyde, methyl tert-butyl ether, methyl benzoate, anisole, peroxyacid derivative, as well as a host to other specialized chemicals.

See also: Methanol, Petrochemicals.

Microalgae

Microalgae are photosynthetic microorganisms that convert sunlight, water, and carbon dioxide to algal biomass.

Microalgae are a diverse group of prokaryotic and eukaryotic photosynthetic microorganisms that grow rapidly due to their simple structure. They can potentially be employed for the production of biofuels in an economically effective and environmentally sustainable manner.

The majority of algae that are intentionally cultivated fall into the category of microalgae (also referred to as phytoplankton, microphytes, or planktonic algae). Macroalgae, commonly known as seaweed, also have many commercial and industrial uses, but due to their size and the specific requirements of the environment in which they need to grow, they do not lend themselves as readily to cultivation.

Microalgae have been investigated for the production of a number of different biofuels including biodiesel, bio-oil, bio-synthesis gas, and bio-hydrogen. The production of these biofuels can be coupled with flue gas carbon dioxide mitigation, wastewater treatment, and the production of high-value chemicals. Microalgae farming can also be carried out with seawater using marine microalgal species as the producers. Developments in microalgal cultivation and downstream processing (e.g., harvesting, drying, and thermochemical processing) are expected to further enhance the cost-effectiveness of the biofuel from microalgae strategy.

Microalgae can provide several different types of renewable biofuels. These include methane produced by anaerobic digestion of the algal biomass, biodiesel derived from microalgal oil, and photobiologically produced biohydrogen. The idea of using microalgae as a source of fuel is not new, but it is now being taken seriously because of the escalating price of crude oil and, more significantly, the emerging concern related to global warming that is associated with burning fossil fuels.

See also: Biomass, Macroalgae.

Microchannel Reactor

A microchannel reactor is a reactor that consists of numerous channels with small diameters of less than a few millimeters, and microchannel process technology is used in a range of applications. These include the large number of chemical and process systems that involve thermal processing, ranging from ethane cracking to fuel processing catalytic processes, such as hydrocracking; chemical reactions and production, for example, steam methane reforming and ethylene oxidation; separations, mixing, and emulsification; catalytic processes; gas processing for operations such as hydrogen production; biological and medical applications; and integrated and multi-phase systems. In terms of small-scale distributed biomass-to-liquids production, microchannel reactors offer particular advantages.

For example, because the structure and dynamics of microchannel reactors improves heat transfer between process fluids and channel walls, the biomass-to-liquids process is intensified. In addition, microchannel reactors also allow the use of more active catalysts than conventional systems, which greatly increases the throughput per unit volume of the reactors. The use of microchannel process technology offers a number of advantages in a range of energy and chemical processing applications. These include: (i) improved heat transfer properties and (ii) higher energy efficiency. Microchannel has thin reaction channels which greatly improves heat and mass transfer. This allows optimal temperature control across the catalyst bed, which maximizes catalyst activity and life.

See also: Fischer-Tropsch Process, Reactor Types.

Mill Residue

Mill residues include bark, coarse residues (chunks and slabs), and fine residues (shavings and sawdust) generated at sawmills that process harvested wood. Primary mill residues tend to be clean, uniform, concentrated, and of low moisture content; most of these materials are already used for products or boiler fuel at the mills.

Mill residue, including chips, sawdust, shavings, and bark, is generated in the process of producing primary wood products. The major primary wood products produced in East Texas include lumber, plywood, veneer, chips, and

posts/poles. Chips as a primary product are produced from pulpwood roundwood; while residue chips are produced from the tops of sawlogs that are used for producing lumber, veneer, or plywood. Sawdust is produced from sawing lumber from sawlogs, and shavings are produced from lumber surfacing. All primary products have bark as mill residue.

The composition varies by mill, but can be as much as 50% solids to 50% water (in the case of paper mill residue, which is classified as lignocellulosic biomass).

Applicable biorefining processes for mill residue are (i) anaerobic digestion, (ii) gasification, (iii) combustion, (iv) fermentation, (v) fiber composite manufacturing, and (vi) thermochemical liquefaction.

See also: Biomass, Logs And Woodchips, Logging Residue, Wood.

Minerals

Minerals are substances formed naturally in the Earth, and they are composed of elements and have a definite chemical composition and structure. Typically, using geology and mineralogy as the guideline, a mineral or mineral species is a solid chemical compound with a fairly well-defined chemical composition and a specific crystal structure that occurs naturally in pure form.

The definition has been further clarified by the International Mineralogical Association to classify a mineral as (i) it must be a naturally occurring substance formed by natural geological processes, (ii) it must be a solid substance in its natural occurrence – a major exception to this rule is native mercury which is still classified as a mineral by the International Mineralogical Association, even though it crystallizes only below -39°C (-38°F), because it was included before the current rules were established, (iii) it must have a well-defined crystallographic structure, and (iv) it must have a fairly well-defined chemical composition.

The exceptions to this definition are the fossil fuels resources that are often classed (in the United States and Canada) among the mineral resources of the country, the state, or the province. However, the United States and Canada are not alone in this expansion of the definition of minerals; many other countries also class the fossil fuel as mineral resources.

Using the geological and mineralogical definition gives rise to more than 3,000 minerals known of which some minerals are rare and precious such as gold and diamond, while others are more ordinary, such as quartz (silica, SiO_2). Approximately 99% of the minerals making up the crust of the Earth are made up of just eight elements. Most of these elements are found combined with other elements as compounds. Minerals are elements or compounds that occur naturally in the crust of the Earth. Rocks are mixtures that are composed of minerals and just as elements are the building blocks of minerals; minerals form the building blocks of rocks.

Minerals are naturally-occurring inorganic solids with well-defined crystalline structures resulting from definite internal structures and composition (Wenk and Bulakh, 2004; Mills et al., 2009; Rafferty, 2011). Minerals are most commonly associated with rocks due to the presence of minerals within the rocks. And these rocks may consist of one type of mineral, or may be an aggregate of two or more different types of minerals that are segregated into separate phases or strata. Silicate minerals comprise approximately 90% of the crust of the Earth. Other important mineral groups include (alphabetically and not in order of abundance): carbonates, halides, native elements, oxides, phosphates sulfates, and sulfides.

Thus, a mineral is formed by a natural process and anthropogenic compounds are excluded. In addition, a mineral is typically abiogenic and does not result from the activity of living organisms. Biogenic substances are chemical compounds produced entirely by biological processes without a geological component and therefore not regarded as minerals. However, if geological processes were involved in the genesis of the compound, then the product can be accepted as a mineral.

Mineral resources have been known and developed throughout historical time, especially ores containing copper (James and Thorpe, 1994). Mineral deposits, including ore bodies and potential ore, can be developed to provide economically valuable commodities (Bain 1987). Therefore, extraction and maximum use must be planned for the benefit of the largest number of people. Such a policy is known as conservation, and it is influenced by many economic and political factors. As costs increase, people tend to use less; they retain materials for more essential uses, thus practicing conservation.

For convenience, raw materials are classified as fuels (see above), metals (including ferrous metals, nonferrous metals, light metals, as well as precious metals), and industrial minerals or nonmetallic elements and have a variety of uses. It is because of these various uses that metals find their way into the environment. The increased demand for a particular metal, coupled with the necessity to utilize lower grade ores, has a significant effect upon the amount of ore that must be mined and processed to produce a unit of a product. Typically, in many industries for every unit of the product, a leaner ore will produce more units of byproducts, some of which can be used and some of which cannot because of the tendency for the by-products to be unusable thereby requiring discharge to the land and/or water systems and the accompanying environmental consequences.

A number of minerals other than those used to produce metals are also important sources of industrial and domestic products. For example, clays, which occur as suspended and sedimentary matter in water and as secondary minerals in soil, are also used for clarifying oils, as catalysts in crude oil processing, as fillers and coatings for paper, and in the manufacture of firebrick, pottery, sewer pipe, and floor tile.

Fluorine compounds are widely used in industry; for example, fluorspar (CaF_2) is used in large quantities as a flux in steel manufacture. Freon-12 (difluorodichloromethane, CF_2Cl_2) is widely used as a refrigeration and air-conditioning fluid and is considered to be a major stratospheric pollutant. Sodium fluoride is used for water fluoridation.

Mica is a complex aluminum silicate mineral which is transparent, tough, flexible, and elastic. Better grades of mica are cut into sheets and used in electronic apparatus, capacitors, generators, transformers, and motors. Finely divided mica is widely used in roofing, paint, welding rods, and many other applications. Phosphorus, along with nitrogen and potassium, is one of the major fertilizer elements. Many soils are deficient in phosphate. The non-fertilizer applications include supplementation of animal feeds, synthesis of detergent builders, and preparation of chemicals such as pesticides and medicines.

Sulfur can exist in many forms which undergo a complicated cycle (Figure 2.4). Sulfur may be expelled from volcanoes as sulfur dioxide or as hydrogen sulfide, which is oxidized to sulfur dioxide and sulfates in the atmosphere. Highly insoluble metal sulfides are oxidized upon exposure to atmospheric oxygen to relatively soluble metal sulfates.

In the ground and in water, sulfate (SO_4^{2-}) is converted to organic sulfur by plants and bacteria. Bacteria mediate transitions among sulfates, elemental sulfur, organic sulfur, and hydrogen sulfide. Sulfur may either escape to the atmosphere (usually as the oxides) and reappear in the form of sulfurous and sulfuric acids in rainfall (acid rain) or be retained as metal sulfides. In fact, the four most important sources of sulfur are (in decreasing order): deposits of elemental sulfur, hydrogen sulfide recovered from sour natural gas, organic sulfur recovered from crude oil, and pyrite (FeS_2).

The development of large machines for handling huge tonnages of rock and the use of refined explosives have improved mining methods, as illustrated in many coal mining operations and in the mining of oil sand. Open-pit and strip mines are larger and more efficient than ever before, and lower grades of ore are being recovered. It is common for a mine to produce 50,000 tons (45,000 metric tons) of ore a day, and some yield more than 100,000 tons (90,000 metric tons).

Improved methods of transportation, concentration, and smelting permit less costly handling of large tonnages and improve recoveries. Newer smelting methods are cleaner, have as good or better recovery records, and may prove to be less expensive to operate. And the environmental aspects of mining many of these minerals need attention. Even the simplest mining procedure such as the recovery of gravel for asphalt highways can have important environmental effects.

The increased use and popularity of mineral resources are due, no doubt, to the relative ease of accessibility which has, in many cases, remained relatively unchanged over the centuries. There are exceptions to the ready availability (crude oil is an example) because of various physical and political reasons, although the prognosis for a continuing crude oil industry remains optimistic through cooperation and planning.

The relatively simple means by which many mineral resources can be utilized has also been a major factor in determining their popularity. And many of the commodities produced from mineral resources:

Ore $\rightarrow$ mineral $\rightarrow$ commodity

The ease with which mineral resources (such as the fossil fuels) were available to the world did, indeed, play a major role in their increased use. The conversion of these natural products to usable products and, in some cases,

to valuable chemicals served to increase their popularity, if coal, crude oil, and natural gas can be used as examples. More specific examples are the coal chemicals industry of the 19th century and the petrochemical industry of the 20th century.

There are projections that the era of fossil fuels (gas, crude oil, and coal) will be almost over when cumulative production of the fossil resources reaches 85% of their initial total reserves. Should the same apply to mineral resources in general, then there may be some cause for concern, perhaps alarming and the issue is worthy of some attention. And a major issue is, naturally, the scarcity of the fossil fuel resources that are used as sources of energy as a means of producing valuable products from a variety of non-fossil fuel resources. For example, the scarcity of crude oil (relative to a few decades ago) is real but it seems more than likely that the remaining reserves of crude oil, coal, and natural gas make it likely that there will be an adequate supply of energy for several decades.

Therefore, technologies to ameliorate the effects of the technologies that are employed in developing the mineral resources must be pursued vigorously. There is a need for on-line analysis of the various product streams (Breen and DeMarco, 1992) to determine the nature of the effluents before they are released to the environment. There is a challenge that must not be ignored, and the effects of, for example, acid rain on soil and water leave no doubt related to the need to control its causes. Indeed, recognition of the need to address these issues is the driving force behind recent energy strategies as well as a variety of research and development.

Miscanthus

Miscanthus (also called silvergrass or silver grass) is a hardy perennial grass that produces a crop of bamboo-like cane up to 15 feet tall. *Miscanthus* is high in lignin and lignocellulose fiber and uses the C4 pathway. It can be grown in a cool climate and on many types of arable land. *Miscanthus* does not require a big input of fertilizers due to its capability to recycle large amounts of nutrients. *Miscanthus* has a similar calorific value per unit weight as wood and therefore could possibly be used in the same power plant or those designed for agricultural residues.

Miscanthus can (theoretically) give an annual harvest of up to 12 tons per acre of dry matter excluding the first couple of years. Like other bioenergy crops, the harvested stems of *miscanthus* may be used as fuel for production of heat and electric power, or for conversion to other useful products such as ethanol. *Miscanthus* is high in lignin and lignocellulose fiber and uses the C4 pathway. It can be grown in a cool climate and on many types of arable land. *Miscanthus* does not require a large input of fertilizers due to its capability to recycle large amounts of nutrients. Once established, the crop can be harvested annually for at least 15 years. By the third year, harvestable yields are between 10 to 13 tonnes (1 tonne = 1,000 kilograms = 2,204.6 lbs) per hectare (1 hectare = 2.47 acres).

Miscanthus is usually planted in April, reaches 1-2 meters in height by late August, starts drying by late July, and is harvested in winter. However, after the first year, the grass is not harvested and the yield of the second year can reach maximum 10 t/ha of dry matter. Planting can be carried out using semi-automatic potato planters for plants, bespoke planters, or manure spreaders for crushed rhizomes (the least favored option). Harvesting can be carried out using a number of different machines such as a mower conditioner or forage harvester to cut the grass, balers to bale the product, and transport with conventional transportation. *Miscanthus* also can be harvested every year with a sugar cane harvester.

Miscanthus is well equipped for high productivity under relatively cool temperatures and may require substantial amounts of water for maximal growth (its growth could therefore also have valuable environmental benefits by acting as absorbing disposal areas for wastewater and some industrial effluents). Furthermore, *Miscanthus* seems to grow well in most soil conditions (bar thin droughty soils) but appears to thrive within areas which are currently best-suited to maize production. The advantages of *Miscanthus* as an energy crop are that it multiplies very rapidly, has a high yield which is relatively dry, and can be harvested annually (from its second season onwards) compared with every 2 to 4 years for short rotation coppice. Further advantages are that *Miscanthus* can be grown and harvested with existing farm machinery, it requires little or no pesticide/fertilizer input after establishment, and the harvest can use the same infrastructure for storage and transport as short rotation coppice. Finally, *Miscanthus* has a

similar calorific value per unit weight as wood and therefore could possibly be used in the same power plant or those designed for agricultural residues.

See also: Short Rotation Coppice.

Miscibility

An equilibrium condition, achieved after mixing two or more fluids, which is characterized by the absence of interfaces between the fluids and involves (i) first-contact miscibility: miscibility in the usual sense, whereby two fluids can be mixed in all proportions without any interfaces forming; an example is at room temperature and pressure, ethyl alcohol and water are first-contact miscible. (ii) multiple-contact miscibility (dynamic miscibility): miscibility that is developed by repeated enrichment of one fluid phase with components from a second fluid phase with which it comes into contact, and (iii) minimum miscibility pressure: the minimum pressure above which two fluids become miscible at a given temperature, or can become miscible, by dynamic processes.

See also: Incompatibility, Stability and Instability.

Mixalco Process

The MixAlco process is an alternative biochemical route for the production of mixed alcohols. In the process, biomass feedstock is mixed with water and pretreated with hydrated lime $[\text{Ca}(\text{OH})_2]$ followed by fermentation using acid-forming microbes which form carboxylic acids. This is followed by addition of calcium carbonate (CaCO_3) which neutralizes the solution and forms dilute carboxylate salts. The salts are then dried and sent to a heated reactor where they are converted to ketones (e.g., acetone), releasing calcium carbonate. Finally, the ketones are hydrogenated to mixed alcohols, predominately propanol, butanol, and pentanol.

The fermentation stage is relatively slow (140-day solids retention time and 14-day liquid retention time) which requires a large reactor volume. To keep costs low, the fermentation stage is envisioned as a covered and lined in-ground lagoon or landfill with recirculating hydrated lime solution. Hydrogen needs to be added at a rate of approximately 0.17 pounds per gallon of alcohol (or 2.6% of final weight). In a full-scale system, mixed alcohol production is estimated to be approximately 60 gallons per dry ton of post-sorted feedstock.

See also: Alcohols, Butanol, Ethanol, Methanol, Propanol.

Mixing

Mixing (sometimes referred to as agitation or blending) is a unit operation widely used in various processes and is an operation in which a uniform combination of two or more components is formed. In addition to blending components together, mixing operations may bring about other desirable changes in the materials being mixed, such as (i) mechanical working, (ii) promotion of heat transfer, and (iii) facilitating chemical or biological reactions such as in fermentation. The components in a mixing operation may be liquids, pastes, dry solids, or gases. The degree of uniformity attainable in a mixing operation varies, depending on the nature of the components. In the case of low-viscosity miscible liquids or highly soluble solids in liquids, a high degree of uniformity is attainable. Less intimate mixing is likely to occur in the case of viscous liquids, pastes, and dry solids. Combining immiscible materials together usually requires specialized equipment. Efficient utilization of energy is another criterion of mixing. This is more easily attainable in the case of low-viscosity liquids as compared with pastes and dry solids.

The various types of mixers in common use are (i) the paddle mixer, (ii) the turbine mixer, and (iii) the propeller mixer. A paddle mixer or mixer consists of a flat blade attached to a rotating shaft, which is usually located centrally in the mixing vessel. The speed of rotation is relatively low, in the range 20 to 150 rpm. The blade promotes rotational and radial flow but little vertical flow. It is usually necessary to fit baffles to the mixing vessel. Two or four blades may be fitted to the shaft. A turbine mixer has four or more blades attached to the same shaft,

which is usually located centrally in the mixing vessel. The blades are smaller than paddles and rotate at higher speeds, in the range 30 to 500 rpm. Simple vertical blades promote rotational and radial flow. Some vertical flow develops when the radial currents are deflected from the vessel walls. A propeller mixer consists of a relatively small impeller, similar in design to a marine propeller, which rotates at high speed, up to several thousand rpm. It develops strong longitudinal and rotational flow patterns. If mounted on a vertical shaft and located centrally in the mixing vessel, baffling is essential. Alternatively, the shaft may be located off center in the vessel and/or at an angle to the vertical.

When mixing highly viscous and paste-like materials, as might be the case in many biomass-to-products processes, it is not possible to create currents which will travel to all parts of the mixing vessel, as happens when mixing low-viscosity liquids. Consequently, there must be direct contact between the mixing elements and the material being mixed. The mixing elements must travel to all parts of the mixing vessel, or the material must be brought to the mixing elements. Mixers for such viscous materials generally need to be more robust, have a smaller working capacity, and have a higher power consumption than those used for liquid mixing. The speed of rotation of the mixing elements is relatively low and the mixing times long compared to those involved in mixing liquids.

Mobile Bed Scrubber

The mobile bed scrubber was designed to clean various gas streams (including coal gas and flue gas) and consisted of thousands of ping-pong-ball-sized hollow hard plastic spheres that were enclosed in cages made from stainless steel rods. Above the mobile bed was a single level of sprays that distributed the scrubbing slurry over the bed. Above the spray header was a mist eliminator. The base of the absorber consisted of a series of pyramidal hoppers, and the discharge from each hopper was the suction to an absorber recycle pump.

The hot gas inlet was between the hopper and the bottom of the mobile bed. To maintain the balls in suspension, gas velocity in the absorber was critical. If the gas velocity was too high, the mobile packing pressed against the top of the cage, causing the scrubbing slurry to accumulate on top of the packing until there was enough head to break through. A gas velocity that was too low caused a similar situation on the bottom of the cage.

Abrasion of the mobile packing was a significant problem. The original, blow-molded hard plastic spheres had a seam which was a weak point, and was subject to wear from the fly ash in the slurry and from rubbing against other spheres. Eventually, the abrasion was sufficient for the spheres to separate at the seam. The half-spheres dropped through the cage rods and into the slurry, where their sharp edges cut the lining of the piping and pumps. UOP then developed a soft plastic sphere the same size as the original spheres. As these balls heated up to the adiabatic saturation temperature of the scrubber, the pores in the spheres would expand letting some of the air contained in the sphere out. This was not a problem until the system was shut down and the spheres cooled to the ambient temperature. No longer maintaining a spherical shape because the air inside the sphere had escaped, they would collapse and drop through the cage rods and get into the scrubbing slurry.

These soft plastic spheres would be found all over the plant site! Some were able to work their way through the mist eliminator blades and then exit the chimney. Others would enter the blowdown and be found floating on the thickener or in ponds.

See also: Gas Cleaning.

Mobil-M Process

The Mobil M process was developed by Mobil Oil Corporation for the purpose of converting methanol directly into high-octane gasoline.

In this process, methanol is first dehydrated to yield dimethyl ether, followed by further dehydration to yield a series of hydrocarbon products:



The distribution of hydrocarbon products is controlled by the zeolite catalyst (a crystalline aluminosilicate with pores, or cavities – the size and geometry of the zeolite pores that control product distribution). Molecules with critical dimensions larger than the pore size cannot be made in the process. Both fixed-bed and fluidized-bed reactors have been employed in developing the Mobil M process.

The crude methanol is vaporized and fed to the first converter stage at approximately 300°C (570°F) and 300 psi where it is catalytically converted to an equilibrium mixture of dimethyl ether, methanol, and water by the reaction:



The first stage product is then combined with a recycle stream and led to the second-stage converter. The inlet temperature is approximately 345°C (650°F), and the outlet temperature is approximately 400°C (750°F). The second-stage converter, filled with catalyst, produces gasoline constituents. The raw product is fractionated, the light ends alkylated, the naphtha recovered from the conversion steps is hydrotreated, and the products blended to produce a gasoline with a 92 research octane-clear (RON) rating.

In the methanol-to-gasoline process, methanol is passed in the vapor phase upward through a catalyst bed at 415°C (775°F) and at 25 psi whereupon the methanol is converted to hydrocarbon derivatives and water. The catalyst is removed from the products at the top of the reactor, and overhead product then condensed and separated from the water; small quantities of coke may also be produced. Some degree of catalyst regeneration is necessary from time to time.

A key characteristic of the M-Gasoline Process is the ability of the catalysts to selectively produce high-octane gasoline constituents. This selectivity is greater than that obtained from classical Fischer-Tropsch-type catalysts. To illustrate, the gasoline selectivity using Mobil catalysts is stated to be as high as 85%, whereas that from Fischer-Tropsch is of the order of 40 to 50%.

See also: Methanol-to-Gasoline.

Moisture in Biomass

Moisture content is the most important characteristic affecting the quality of biomass fuel for thermal processes like combustion, gasification, and pyrolysis. Materials with lower moisture content cost less to transport and can reduce the size of handling, processing, and energy conversion equipment needed for biomass power because a smaller volume of feedstock would be required to meet the fuel requirements for a plant. On the other hand, high moisture content is desirable for a microbial fermentation process, where a liquid water medium is essential.

Moisture content can be measured on a wet or a dry basis. The wet basis method, in which the moisture content is expressed as a percentage of the total weight, is usually used in engineering calculations. In forest product calculations, the dry basis method is used, in which the moisture content is expressed as a percentage of the dry weight of the wood.

The moisture content of freshly harvested forest and crop residue typically varies from 40% to 60% by weight, and can be higher, especially if the residue is exposed to precipitation. The moisture content of crop residue, such as cereal straws, can be reduced to 15% or less by open air solar drying. By contrast, wood residue typically ranges from 18% to 25% MC or more after air-drying for approximately one year, depending on climate, storage conditions, and bulk characteristics. Bark often has lower moisture content than wood. Moisture content can be influenced by weather. Under drought conditions, the moisture content of standing live trees can drop below 20%, adding to the threat of wildfires.

In combustion processes, high moisture content can lead to incomplete combustion, low thermal efficiency, low flame temperatures, excessive emissions, and the formation of tars that could cause slagging problems. Maximum thermal efficiency is achieved at zero moisture content, referred to as *oven-dry* or *bone-dry*, but complete drying is often too costly or impractical. Woody and herbaceous biomass with moisture content in the range of 10% to 20% is considered optimal for conventional combustion systems. Low moisture content is especially important for most pyrolytic gasification processes, where variations in the moisture content of the feedstock cause large variations in the quality of the gas product. Drying costs must be weighed against the advantages of handling drier feedstock and incremental improvements in the conversion process. Some fluid-bed combustors, however, are designed to operate with variable moisture content of the feedstock up to 50%. Many large-scale combustion plants operate well with little apparent concern for the effects of moisture content in the biomass feedstock on the combustion process. Pre-treatment involving size reduction and air drying, and/or blending with dry fuel may be adequate and cost-effective for such operations.

Biomass feedstocks with high moisture content have higher transportation costs because a large proportion of the weight being shipped is water. Because of the negative impact of moisture content on combustion processes and increases in delivered feedstock costs, a good rule is to attempt to minimize the moisture content of the feedstock. This can be done by using a blend of feedstocks, including lower moisture content mill residue such as sawdust to offset higher moisture content forest biomass. Alternatively, it is possible to reduce moisture content through passive or active drying. For ethanol feedstock, the increased delivered costs of biomass with higher moisture content probably outweigh the costs of increased process water requirements, but this needs to be examined on a site-specific basis.

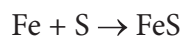
Molten Bath Gasifiers

Unlike combustion processes, gasification is an oxygen-starved process that converts solid fuels (biomass, coal, etc.) into gaseous fuels (Hydrogen and Carbon Monoxide). Gasification is uniquely capable of producing not only heat and power, but also can be used with downstream catalysts to convert the synthesis gas to liquid fuels and chemicals (diesel, ethanol, methanol); and, to hydrogen gas for fuel cell applications.

A number of different carbonaceous feedstocks can be used in gasification process, and, furthermore, the production of synthesis gas enables a number of downstream applications to be integrated with the gasification plant to produce a wide array of products.

Molten bath gasifiers (molten salt gasifiers) use a molten salt as a means of gasifying the carbonaceous feedstocks and may be applicable to biomass gasification.

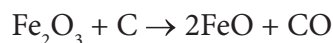
In the CO₂ Acceptor process, the added medium, namely calcined limestone or dolomite, not only provides the heat for gasification, but also improves the quality of the synthesis gas by virtue of its chemical activity. In molten bath gasifiers, the added media is selected mainly for its chemical functions, while the heat requirements are provided autothermally by introduction of oxygen or air directly into the gasifier. Molten iron is frequently advocated as a suitable medium due to the affinity of iron for sulfur:



Although the prime purpose of the added medium is to provide a sulfur-free fuel or synthesis gas, it also serves ancillary functions. It acts as a dispersing medium for the coal; it acts as a heat sink with high heat transfer rates for distributing the heat of combustion; it also physically retains the ash in the coal. In some cases, the medium may also catalyze the gasification reactions.

The Atomics International (AI) and Kellogg gasifiers are examples of reactors that employ sodium carbonate as the molten medium. The sodium carbonate reacts with the sulfur to form compounds that catalyze the partial oxidation of the coal. The sulfur in the molten salt is removed as hydrogen sulfide in the regeneration system, and elemental sulfur may be recovered as a by-product.

Another molten bath gasification process is the Rummel-Otto gasifier, one version of which has been proven commercially in sizes up to 250 t/d of coal. The molten medium in this gasifier is slag. Unlike other molten media gasifiers, the intent is not to remove pollutants from the product gases. Instead, the slag acts more as a heat shield and as a reservoir for oxygen. Iron oxide in the slag accepts oxygen followed by gasification of the carbon by partial oxidation:



The slag further acts as a promoter of the gasification reactions.

The Rummel-Otto gasifier consists of three zones. In the top zone, the product gases are cooled by direct water quench, the middle zone is an entrained flow combustion/gasification zone of the Texaco and Koppers-Totzek type, while the bottom zone is the slag bath. Dried and pulverized coal is entrained in a recycle gas and injected along with steam and oxygen into the gasifier.

The injection nozzles are oriented tangentially above the slag bath, and the entering feed imparts a slow vortex motion to the slag. The turbulence induced in the slag bath by the injected feed enhances mass and heat transfer between the two phases. Lime may be added as a fluxing agent to decrease the viscosity of the slag.

The steam rate is low but sufficient to moderate the flame temperature to approximately 1,650°C (3,000°F). The reactor vessel in the combustion/gasification zone is both refractory lined and water jacketed. Additional heat shielding is provided by the slag bath.

The gases leaving the gasification zone have high carbon monoxide concentrations as is typical for the high oxygen-to-steam feed ratio and high reaction temperature. On entering the quench zone, they react further with water to increase the H_2/CO ratio to approximately about 1. However, approximately 75% of the total water entering the gasifier remains undecomposed, leaving a gas containing more than 40% moisture by volume. The water quench serves to cool the gases to 980°C (1,800°F) before they enter the cyclones where unreacted char is separated and reinjected into the gasifier. The cold gas efficiency for this plant is approximately 80%.

See also: Gasification, Gasification of Biomass, Molten Salts.

Molten Salts

A molten salt is a (solid phase) salt which is solid at standard temperature and pressure (STP) but enters the liquid phases at elevated temperature. A salt that is typically liquid even at standard temperature and pressure is usually called a room temperature ionic liquid, although technically, molten salts are a class of ionic liquids.

In most molten salt energy storage systems, the molten salt is maintained as a liquid throughout the energy storage process. In this form of use, molten salts are typically made up of 60% w/w sodium nitrate and 40% w/w potassium nitrate, and the salts melt at approximately 220°C (400°F). Molten salts are often used with concentrating solar power (CSP) plants to store thermal energy for electricity generation.

Molten salt batteries are a class of primary and secondary electric batteries that use molten salts as the electrolyte and offer both a higher energy density through the careful selection of reactant pairs as well as a higher power density by means of a high-conductivity molten salt electrolyte. The batteries are used in services where high energy density and high power density are required, and these features make rechargeable molten salt batteries a promising technology for powering electric vehicles.

See also: Molten Bath Gasifier.

Municipal By-Products

The term municipal by-products refers to biomass by-products produced by the urban population and comprise two types: solid municipal by-products, and gas/liquid municipal by-products produced in cities and villages.

Solid municipal biofuels comprise by-products produced by the residential, commercial, industrial, public and tertiary sectors that are collected by local authorities for disposal in a central location, where they are generally incinerated (combusted directly) to produce heat and/or power. Hospital waste is also included in this category. Gas/liquid municipal biofuels refers to biofuels derived principally from the anaerobic fermentation (biogas) of solid and liquid municipal wastes which may be land-fill gas or sewage sludge gas. In fact, many countries have reached a critical stage in the management of our two major municipal by-products such as (i) municipal solid waste (MSW), and (ii) biosolids.

Municipal solid waste consists of a variety of components, including paper and cardboard products, yard wastes, as well as metals, plastic, glass, wood, and food waste. The majority of municipal solid waste but is placed in landfills, but recycling and agricultural uses of municipal solid waste are becoming preferable to landfilling. Many of the components of municipal solid waste (paper, yard waste, food wastes, wood products) are biodegradable under the appropriate conditions and may have potential to be used to improve agricultural and nonagricultural land. Because of limitations associated with odors, pathogens, and undesirable chemical and physical properties, new and unstable organic municipal by-products cannot be added directly to the soil. However, composting of biosolids and selected components of municipal solid waste is an effective waste management process.

Composting is a self-heating microbiological process in which the decomposition of organic materials is accelerated by the growth and enzymatic activity of mixed populations of bacteria and fungi. Composting reduces the weight and volume of the byproduct while abating odors, destroying pathogens, and converting nutrients to forms that biosolids and selected components of municipal solid waste have value as biofertilizers and soil conditioners. However, these materials have relatively low nutrient contents and may need to be enriched with inorganic fertilizers to meet plant growth requirements. Municipal by-products add organic matter to soils, thus maintaining and enhancing soil health and productivity.

Standards have been developed, based on concentrations of trace elements and toxic organics, to regulate land application of biosolids. Currently, the majority of wastewater biosolids are applied to land. Similar regulations are needed for land application of the components of municipal solid waste. The fate and subsequent bioavailability of nutrients, metals, and synthetic organic residues during and after composting of municipal solid waste components will have to be determined. Composted biosolids and municipal solid waste may have potential uses in the horticulture industry as growth media and for biocontrol of soilborne plant diseases. Compost quality and maturity criteria need to be developed to enhance the horticultural uses of municipal by-products.

See also: Municipal Solid Waste, Waste.

Municipal Solid Waste

Municipal solid waste (MSW) consists of a variety of items ranging from organic food scraps to discarded furniture and appliances.

Municipal solid waste is a waste type that includes predominantly household waste (domestic waste) with sometimes the addition of commercial wastes collected by a municipality within a given area. They are in either solid or semisolid form and generally exclude industrial hazardous waste. The term residual waste relates to waste left from household sources containing materials that have not been separated out or sent for reprocessing.

Municipal solid waste is a source of energy probably with as much potential as wood. Non-organic constituents such as metals and glasses must be removed, and may be sold for their recycle value to compensate for the cost of the separation step at least partly. The remaining refuse contains a high proportion of cellulosic material (paper) and other components not readily amenable to biochemical conversion. The characteristics of municipal solid waste can vary significantly with the time of the year, which further detracts from its suitability for biochemical conversion. There are also variations in the constituents, many of which are classed as hazardous (Table M-3).

Table M-3 Examples of toxic constituents in municipal solid waste.

Name*	Formula/symbol	Concern
Non-Metals		
Arsenic	As	Carcinogen and mutagen
Selenium	Se	Long-term toxin
Metals		
Barium	Ba	Long-term circulatory system effects
Cadmium	Cd	Toxic – a carcinogen
Chromium	Cr	Hexavalent compounds are carcinogens and corrosive
Copper	Cu	Toxic by ingestion or inhalation of dust and fumes
Lead	Pb	Toxic by ingestion or inhalation of dust and fumes
Mercury	Hg	Highly toxic by skin absorption and inhalation of vapor
Nickel	Ni	Long-term central nervous system disorders
Silver	Ag	Toxic metal; long-term effects
Organic compounds		
Benzene	C_6H_6	Carcinogen; highly toxic; flammable
Ethyl benzene	$C_6H_5CH_2CH_3$	Toxic by ingestion, inhalation, and skin
Toluene	$C_6H_5CH_3$	Flammable dangerous fire risk. Toxic
Halogenated compounds		
Chlorobenzene	C_6H_5Cl	Moderate fire risk; toxic by inhalation and ingestion
Chloroethylene	CH_2CHCl	Extremely toxic and hazardous ~ all avenues
Dichloromethane	CH_2Cl_2	Carcinogen and narcotic
Tetrachloroethane	$CHCl_2CHCl_2$	Possible carcinogen

*Listed alphabetically within each category.

Wood and yard and tree trimmings are the two sources within this residue stream that are potentially recoverable for energy use. The wood component includes discarded furniture, pallets, containers, packaging materials, lumber scraps (other than new construction and demolition), and wood residuals from manufacturing.

Thermal processes are consequently of interest. Direct combustion for district heating is an obvious application practiced in some countries, while gasification is another possibility. Of particular interest is a scheme for mixing coal, municipal solid waste, and dewatered sewage sludge to produce briquettes suitable for gasification. Apart from supplementing the coal energy, the waste material renders the coals non-caking. Appropriation of these waste materials for energy is not competitive with other uses, and in fact reduces their disposal problem. An additional advantage over other biomass resources is that collection or “harvesting” procedures are both established and financed.

In principal, biomass resources can be converted using any one of a variety of conversion processes. However, depending on their composition and other properties discussed above, some processes can be expected to be more effective than others in recovering energy from a specific resource.

The process/biomass combinations offer a high potential, and in cases where more than one process is suitable, the end product will be an important consideration in selecting among conversion routes. Liquid products are more

versatile than gas and heat. Methanol is not as well suited as ethanol for blending with gasoline to form gasohol, but may prove to be an acceptable stand-alone fuel.

There are six general categories of municipal solid waste which are (i) biodegradable waste such as food and kitchen waste, green waste, paper – which can also be recycled, (ii) recyclable material such as paper, glass, bottles, cans, metals, and certain plastics, (iii) inert waste such as construction and demolition waste, dirt, rocks, and debris, (iv) composite waste which includes waste clothing and waste plastics such as toys, (v) domestic hazardous waste (also called household hazardous waste), and (vi) toxic waste such as discarded medication, paint, chemical, light bulb, fluorescent tube, spray cans, fertilizer and pesticide containers, batteries, and shoe polish.

There is also electronic waste which is a waste consisting of any broken or unwanted electrical or electronic appliance. While there is no generally accepted definition of electronic waste, in most cases, electronic waste consists of electronic products that were used for data processing, telecommunications, or entertainment in private households and businesses that are now considered obsolete, broken, irreparable, or of no further use due to planned obsolescence. Despite its common classification as a waste, disposable electronics are a considerable category of secondary resource due to their significant suitability for direct reuse (for example, many fully functional computers and components are discarded during upgrades), refurbishing, and material recycling of its constituents.

See also: Biomass, Waste.

Municipal Solid Waste – Energy From

The recovery of energy from municipal solid waste (MSW) in its simplest manner has existed for centuries. The burning, or incineration, of wastes such as wood waste and miscellaneous household products, was first used to produce warmth.

In addition, to incineration (which produced a given amount of energy – Table M-4) gaseous fuels can also be obtained by anaerobic digestion in conjunction with landfill gas recovery.

Table M-4 Comparison of heating values of various waste-derived fuels.

Fuel Source	Btu/lb
Yard Wastes	3,000
Municipal solid waste	6,000
Combustible paper products	8,500
Textiles and plastics	8,000
Bituminous coal (average)	11,300
Anthracite coal (average)	12,000
Spent tires	13,000-15,000
Crude oil (average)	17,000
Natural gas (425 ft ³)	13,500

One method of recovering usable energy from MSW is gasification in which the waste material is gasified under high pressure by the injection of air and steam with concurrent gas/solid flow. After separation of the non-combustible waste, water or oil is added to the combustible municipal solid waste to form a pumpable slurry. The resulting slurry is then pumped under pressure to the gasifier. In the gasifier, the slurry is reacted with air at high temperatures. The resultant gaseous product is then sent to a scrubbing system to remove any pollutants and impurities.

Anaerobic digestion of solid waste is a process similar to that used for biogas production. Anaerobic bacteria, in the absence of oxygen, are used to break down the organic matter of the waste. Frequently, the municipal solid waste is mixed with sewage sludge from the treatment plant to enhance the efficiency of the digestion and the production of a mixture of methane and carbon dioxide gases – the typical ratio of the gas mixture is 70% methane and 30% carbon dioxide, and the gas mixture has a heating value on the order of 650 to 750 BTU/ft³.

Pyrolysis of municipal solid waste has also been used to generate a gaseous fuel. However, pyrolyzing a cellulose-based waste atmospheric pressure will generate a liquid fuel.

A typical pyrolytic reaction for the cellulose component of municipal solid waste may be written as:



The formula $\text{C}_6\text{H}_8\text{O}$ represents a family of liquid products, but the actual composition of $\text{C}_6\text{H}_8\text{O}$ is dependent on the feedstock composition and the reaction temperature.

When the pyrolysis temperature is higher than 350°C (660°F), small quantities of polyethylene chips can be added to the cellulose feedstock. Operating temperatures ranging from 100 to 400°C (210 to 750°F) decrease the amount of gaseous product and increase the formation of the liquid product.

In addition to the liquid fuel or oil, pyrolysis generates a medium-BTU gas stream that, after purification, can be recycled as a supplemental fuel within the plant. Process water and char are also generated. The process water may have to be treated before discharge, or can be used in the plant as heat exchanger water. All of the pyrolysis products have the potential of being useful fuels or intermediates for producing other valuable products for use in the petrochemical industry.

Although there are a number of MSW-derived fuel systems in full operation and/or being started up throughout the world, there are still developmental issues in regard to process design and engineering, pollution control and monitoring, equipment design and selection, and application-related information. The cost-to-benefit analysis along with the environmental impact analysis must be carefully conducted for any chosen process and site.

See also: Biogas, Gasification, Gasification of Biomass, Landfill, Landfill Gas, Municipal Waste.

Municipal Waste

Municipal waste (sometimes, depending upon the composition referred to as municipal solid waste, MSW), commonly known as trash or garbage in the United States and rubbish in the United Kingdom is a waste type consisting of everyday items that are discarded by the public. Although the waste may originate from a number of sources that has nothing to do with a municipality, the traditional role of municipalities in collecting and managing these kinds of waste have produced the particular term municipal waste, which often includes wastes of similar character from shops, market and offices, open areas, and treatment plant sites (Table M-5)

Table M-5 Sources of municipal waste

Source	Types
Residential	Food waste
	Garbage
	Ash
	Hazardous waste
Commercial	Food waste
	Garbage
	Ash
	Demolition waste
	Construction waste
	Treatment plant sludge
	Hazardous waste

In order to develop frameworks within which effective waste management strategies can be planned, it is essential to know not only the amounts of waste generated and their sources, but also the type of materials in each waste stream, their properties, potential toxicity, and the hazards they pose to human health and the environment. The lack of reliable time series on solid waste streams and rapid changes in the composition of waste streams are a serious impediment to setting priorities in solid waste management in many developed as well as developing countries.

Municipal wastes in developing countries have a higher proportion of organic matter and ash, higher moisture content, and lower paper content, although refuse from the wealthier suburbs is similar in composition to West European wastes. Organic matter and ash may account for between 60 and 85% of all wastes in low income settlements.

However, despite the large amounts of waste produced by individuals in the wealthy industrialized nations, municipal wastes account for a small proportion of total wastes generated.

Changes in the composition of municipal wastes in developed countries have undoubtedly taken place both at the community and national levels, but data are still relatively sparse. In general, the proportion of ash and grit has decreased, while the proportion of plastics has been growing.

An important component of domestic wastes in industrialized countries is the “bulky” or “consumer durables” wastes, e.g., cars, refrigerators, and washing machines. The number of items discarded each year is growing as rapid changes in technology and production of new models reduces what is perceived to be their useful life.

See Biomass, Municipal Solid Waste, Waste.

Muon

The muon (formerly referred to as a mu meson) is an elementary particle that is similar to the electron with an electric charge of $-1 e$ and a spin of $\frac{1}{2}$ but with a much greater mass. The muon is not known to have any substructure – that is, it is not thought to be composed of any simpler particles. The muon is an unstable subatomic particle with a lifetime on the order of 2.2 microseconds – a microsecond is a unit of time equal to one millionth (0.000001 or 10^{-6}) of a second.

As with the decay of the non-elementary neutron (with a lifetime on the order of 15 minutes), muon decay is slow (by subatomic standards) because the decay is mediated only by the weak interaction because the mass difference between the muon and the set of its decay products is small. Muon decay almost always produces at least three particles, which must include an electron of the same charge as the muon and two types of neutrinos.

Like all elementary particles, the muon has a corresponding antiparticle of opposite charge ($+1 e$) but equal mass and spin – the antimuon (also called a *positive muon*). Muons are denoted by μ^- and antimuons by μ^+ . Muons were formerly called *mu mesons*, but are not classified as mesons.

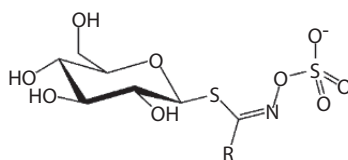
See also: Position, Proton.

Mustard Seed

Mustard (*Brassica juncea*) is the common name for multiple species in the *Brassica* genus. The species of which most people are aware is yellow mustard, referred to as white mustard in Europe, and is grown primarily for condiment mustard seed. As a result, it does not have as high oil content as the other commonly known Indian mustard referred interchangeably in commerce as brown or oriental mustard. *Juncea* varieties are grown for edible leaves or greens or for condiment mustard, and have been and are increasingly grown as an oilseed crop.

The crops commonly called rapeseed and canola in commerce are also in the *Brassica* genus, and are *Brassica napus* species. As a result, they are closely related to *juncea*. Because canola is not a botanical term, but one used to describe compositional qualities, the term is often used with *juncea* when discussing cultivars that have been developed for the oilseed market. Canola varieties of *napus* and canola-type *juncea* have similar compositional characteristics but different crop or agronomic qualities. In theory, oils from both species have the same acid profiles (high in mono-saturate derivatives and low in saturate derivatives) and oil characteristics (lower pour and melting point and better cold flow properties) and similar meal properties (a protein content on the order of 35 to 40% w/w) with low

glucosinolate levels – glucosinolate derivatives are the natural components of many pungent plants such as mustard, cabbage, and horseradish).



Glucosinolate structure

The key differences between *napus* and canola-type *junceae* lie in the agronomic characteristics. Both are an annual, cool season crop, but *junceae* tolerates high temperatures and drought better than *napus*, and thus is better suited for the warmer, drier climates of the Upper Plains of the United States.

Although pure mustard oil is banned for use as a vegetable oil in many countries, it is often applied topically and used as a massage oil, skin serum, and hair treatment. However, in the current context, mustard oil contains approximately 20 to 28% w/w oleic acid, 10 to 12% w/w linoleic acid, 9.0 to 9.5% w/w linolenic acid, and 30 to 40% w/w erucic acid, which leaves an option for the oil as a starting material for the production of alternative fuels.

See also: Biodiesel, Fatty Acids.

Naft

Naft is the pre-Christian era (Greek) term for naphtha, which was the main constituent of Greek fire, which was one of the most effective thermal devices, although it was extremely dangerous for the users. A combustible liquid, it could be shot from siphons or catapults, and it bursts into flames on impact. First developed by the Byzantines in the 7th century, it was later used by the Turks during the Crusades, and was probably first used in Western Europe in the 12th century. Early experiments by the Byzantines in the 6th century used a mixture of sulfur and oil, which would have been terrifying if not destructive. Various versions seem to have existed, and the recipes were frequently kept secret and the exact composition is still speculative.

The incendiary liquids of the ancient and medieval periods have their modern equivalents. World War I saw the development of the flamethrower, a modern version of the Byzantine siphons for discharging Greek fire, which used gas under pressure to squirt a mixture of inflammable oil and petrol, ignited by a burning taper. The twentieth century and the latter half saw the development and use of napalm, an incendiary liquid formed in part from naphtha (naft).

Naphtha

Naphtha is a generic term applied to refined, partly refined, or unrefined mixture of flammable liquid hydrocarbons, the majority of which distills below 240°C (464°F); the volatile fraction of crude oil which is used as a solvent or as a precursor to gasoline. Naphtha normally refers to, i.e., a distillation product from crude oil or boiling in a certain range and containing certain hydrocarbons, a broad term encompassing any volatile, flammable liquid hydrocarbon mixture. In fact, the generic name naphtha describes a range of different products that satisfy the boiling range (and other physical properties) that can be produced from alternate energy sources) that can be used in different applications and produced by various processes (Table N-1).

Table N-1 Naphtha production by various crude oil refining processes.

Process	Primary product	Secondary process	Secondary product
Atmospheric distillation	naphtha		low-boiling naphtha
			high-boiling naphtha
	gas oil	catalytic cracking	naphtha
	gas oil	hydrocracking	naphtha
Vacuum distillation	gas oil	catalytic cracking	naphtha
		hydrocracking	naphtha
	residuum	coking	naphtha
		hydrocracking	naphtha

Naphtha is used primarily as a gasoline blend stock as well as for producing a high octane gasoline component (via the catalytic reforming process). It is also used in the petrochemical industry for producing olefins in steam crackers and in the chemical industry for solvent (cleaning) applications.

The origin of the word naphtha is unclear, having been borrowed by the ancient Greeks from the Old Persian words nafta, naft, and neft, which were used to describe bubbling oil. Naphtha may also have been derived from the

name of the Vedic Hindu and Avestic god Apam Napat, a form of Agni, or fire god. In older usage, naft or neft simply meant crude oil and the words still find use in some languages.

Naphtha is obtained from crude oil as one of the intermediate products from distillation. It is a liquid intermediate between the gases in the crude oil and the higher-boiling kerosene.

The molecular weight range for naphtha constituents is 100 to 215 g/mol; the specific gravity range is 0.75 to 0.85 g/cm³; the boiling point range is to 165 to 225°C (320 to 430°F); the vapor pressure is <5 mm Hg (<5 torr). Naphtha is insoluble in water; colorless (kerosene odor) or red-brown (aromatic odor) liquid; incompatible with strong oxidizers.

Generally, less dense (low-boiling) naphtha will have a higher paraffin content and is often referred to as *paraffinic naphtha*. The main application for this type of naphtha is as a feedstock in the petrochemical production of olefins. When used as feedstock in petrochemical steam crackers, naphtha is heated in the presence of water vapor, and the absence of oxygen and the primary products of the cracking process are olefins (ethylene, propylene, and butadiene) and aromatics (benzene, toluene).

The more dense (high-boiling) naphtha is usually richer in naphthenes and aromatics, and therefore, this type of naphtha can also be used in the petrochemical industry but is more often used as a feedstock for refinery catalytic reformers where it converts the lower octane naphtha to a higher octane (*reformate*).

In terms of renewable energy sources, the hydrothermal liquefaction process (HTL process) or direct liquefaction is a promising technology to treat waste streams from various sources and produce valuable bio-products such as biocrude oil. A major problem with commercializing the hydrothermal liquefaction processes for biomass conversion is that it remains uneconomical when compared to the costs of diesel or gasoline production. High transportation costs of large quantities of biomass increase production costs, and poor conversion efficiency coupled with a lack of understanding complex reaction mechanisms inhibits growth of the process commercially.

In the hydrothermal liquefaction process, biomass is reacted in liquid water at elevated temperature and pressure. The phase equilibria in the hydrothermal liquefaction process are complicated due to the presence of water, supercritical carbon dioxide, alcohols as well as the so-called biocrude. The biocrude is a mixture with a wide molecular weight distribution and consists of various kinds of molecules. Biocrude oil contains 10 to 13% w/w oxygen and is upgraded by catalytic hydrodeoxygenation in a central facility. Preliminary process studies on the conversion of various biomass types into liquid fuels have indicated that hydrothermal liquefaction is more attractive than pyrolysis or gasification.

The biomass is typically fed to the process as a 25% w/w slurry in water, and is treated at temperatures of 300 to 430°C (570 to 805°F) at varying pressures in the presence of liquid water for 5 to 20 minutes to yield a mixture of gas (mainly carbon dioxide) and synthetic crude oil (sometimes referred to as biocrude). Subsequent processing is necessary of the synthetic crude oil to usable fuel (Goudriaan and Peferoen, 1990).

Biomass, such as wood, with a lower energy density is converted to biocrude with higher energy density, organic compounds including mainly alcohols and acids, gases mainly including carbon dioxide. Water is also a by-product. In the products, carbon dioxide, which is the main constituent of the gas product, can be used to represent all gas produced, and methanol and ethanol represent organic compounds. The weight fraction of each component is assigned on the basis of the data of the vacuum flash of biocrude.

See also: Refining.

Naphthalene and Polynuclear Aromatic Hydrocarbons

Naphthalene is a two-ring condensed aromatic hydrocarbon that is produced during the carbonization of carbonaceous materials that must be removed from the gas stream to avoid plugging of lines and valves in subsequent gas usages. It may be scrubbed from the gas with hydrocarbon (usually wash oil) and then separated by distillation. Another removal method is to reabsorb it in tar. Naphthalene may be extracted in the crystalline form as pure material.

Naphthalene is probably the most abundant component in high-temperature coal tar. The primary fractionation of the crude tar concentrates the naphthalene into oils which, in the case of coke-oven tar, contain the majority (75

to 90% w/w) of the total naphthalene. After separation, naphthalene can be oxidized to produce phthalic anhydride which is used in the manufacture of alkyd resins and glyptal resins and plasticizers for polyvinyl chloride.

Naphthalene and its homologs are less acutely toxic than benzene but are more prevalent for a longer period during oil spills. The toxicity of different crude oils and refined oils depends on not only the total concentration of hydrocarbons but also the hydrocarbon composition in the water-soluble fraction (WSF) of crude oil, water solubility, concentrations of individual components, and toxicity of the components. The water-soluble fractions prepared from different oils will vary in these parameters. The water-soluble fractions (WSF) of refined oils (for example, No. 2 fuel oil and Bunker C oil) are more toxic than the water-soluble fraction of crude oil to several species of fish (killifish and salmon). Compounds with either more rings or methyl substitutions are more toxic than less substituted compounds, but tend to be less water soluble and thus less plentiful in the water-soluble fraction.

Among the polynuclear aromatic hydrocarbons, the toxicity is a function of its di- and tri-aromatic hydrocarbon content. Like the single aromatic ring variations, including benzene, toluene, and the xylenes, all are relatively volatile compounds with varying degrees of water solubility.

There are indications that pure naphthalene (a constituent of moth balls that are, by definition, toxic to moths) and alkyl naphthalene derivatives are from three-to-ten times more toxic to test animals than are benzene and alkylbenzene derivatives. In addition, and because of the low water solubility of tricyclic and polycyclic (polynuclear) aromatic hydrocarbons (that is, those aromatic hydrocarbon derivatives that are higher-boiling – higher molecular weight – than naphthalene), these compounds are generally present at low concentrations in the water-soluble fraction of oil. Therefore, the results of this study and others conclude that the soluble aromatics of crude oil (such as benzene, toluene, ethylbenzene, xylenes, and naphthalenes) produce the majority of its toxic effects in the environment.

Once the acutely toxic lower-boiling compounds have left the aquatic environment through volatilization or degradation, the main concern is chronic effects from higher-boiling and more alkylated polynuclear aromatic hydrocarbons.

Bird species with water habitats are the species most commonly affected by oil spills and releases. Oil itself breaks down the protective waxes and oils in the feathers and fur of birds and animals and disrupts the fine strand structure of the feathers resulting in a loss of heat retention and buoyancy and possible hypothermia and death. Oiled birds often ingest crude oil while attempting to remove the crude oil from their feathers. The effects of ingested crude oil include anemia, pneumonia, kidney, and liver damage, decreased growth, altered blood chemistry, and decreased egg production and viability. Ingestion of the oil can also kill animals by interfering with their ability to digest food. Chicks may be exposed to crude oil by ingesting food regurgitated by impacted adults.

The dynamics of the oil-in-water dispersion (OWD) are complex and have relevance related to potential toxicity or hazard. In comparing the toxicities to marine animals of oil-in-water dispersions prepared from different oils, not only the amount of oil added but also the concentrations of oil in the aqueous phase and the composition and dispersion-forming characteristics of the parent oil must be taken into consideration. In comparing the potential impacts of spills of different oils on the marine biotic community, the amount of oil per unit water volume required to cause mortality is of greater importance than any other aspect of the crude oil behavior.

Several compounds in crude oil products are carcinogenic. The larger and higher- molecular-weight aromatic structures (with four to five aromatic rings), which are the more persistent in the environment, have the potential for chronic toxicological effects. Since these compounds are non-volatile and are relatively insoluble in water, their main routes of exposure are through ingestion and epidermal contact. Some of the compounds in this classification are considered possible human carcinogens; these include benzo(a)pyrene, benzo(e)pyrene, benzo(a)anthracene, benzo(b)fluorene, benzo(j)fluorene, benzo(k)fluorene, benzo(ghi)perylene, chrysene, dibenzo(ah)anthracene, and pyrene.

Mixtures of polynuclear aromatic hydrocarbons are often carcinogenic and possibly phototoxic. One way to approach site-specific risk assessments would be to collect the complex mixture of polynuclear aromatic hydrocarbons and other lipophilic contaminants in a semi-permeable membrane device (SPMD, also known as a *fat bag*), then test the mixture for carcinogenicity, toxicity, and phytotoxicity.

The solubility of hydrocarbon components in crude oil products is an important property when assessing toxicity. The water solubility of a substance determines the routes of exposure that are possible. Solubility is approximately

inversely proportional to molecular weight; lower-boiling hydrocarbons are more soluble in water than higher-molecular-weight compounds. Lower-molecular-weight hydrocarbons (C4 to C8, including the aromatic compounds) are relatively soluble, up to approximately 2,000 ppm, while the higher-molecular-weight hydrocarbon derivatives are nearly insoluble. Usually, the most soluble components are also the most toxic.

Finally, the toxicity of crude oil may be affected by factors such as weathering time or the addition of oil dispersants. *Weathered* crude oil and *fresh* crude oil may have different toxicities, depending on oil type and weathering time.

See also: Alkanes, Cycloparaffin Hydrocarbon derivatives.

Naphthenes

Naphthenes (cycloalkane derivatives, cycloparaffin derivatives) are types of alkane derivatives which have one or more rings of carbon atoms in the chemical structure. Cycloalkanes with a single ring are named analogously to their normal alkane counterpart of the same carbon count: for example cyclopropane, cyclobutane, cyclopentane, and cyclohexane.

Naphthenes are similar to alkanes in their general physical properties, but they have higher boiling points, melting points, and densities than alkanes. Cycloalkanes exhibit a similar low reactivity as alkanes, due to relatively unreactive carbon-carbon and carbon-hydrogen; however, the ring strain can cause induce increased reactivity in cycloalkanes.

The boiling point and densities of naphthenes are higher than those of alkane derivatives having the same number of carbon atoms. Naphthenes commonly present in crude oil are rings with five or six carbon atoms. Examples of naphthenes are (Figure N-1):

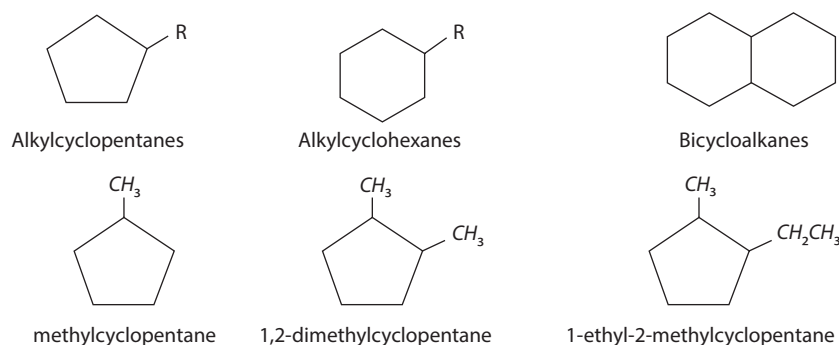


Figure N-1 Examples of naphthene derivatives.

These rings usually have alkyl substituents attached to them (Figure N-1). Multi-ring naphthenes are present in the higher-boiling fraction of crude oil.

See also: Alkanes, Cycloparaffin Hydrocarbons, Refining.

Natural Gas

Natural gas (also incorrectly, in this context, called marsh gas, swamp gas, and landfill gas) is the flammable gaseous mixture that usually occurs with crude oil reservoirs and which provides approximately 24% of the world's energy sources, and the use of natural gas as an energy source is expected to increase over the next several decades.

Natural gas is a mixture of hydrocarbon and small quantities of non-hydrocarbon derivatives that exists either in the gaseous phase or is in solution in crude oil in natural underground reservoirs, and which is gaseous at atmospheric conditions of pressure and temperature (Table N-2).

Table N-2 Range of composition of natural gas.

Constituents	Formula	% v/v
Methane	CH ₄	>85
Ethane	C ₂ H ₆	3-8
Propane	C ₃ H ₈	1-2
Butane	C ₄ H ₁₀	<1
Pentane	C ₅ H ₁₂	<1
Carbon dioxide	CO ₂	1-2
Hydrogen Sulfide	H ₂ S	<1
Nitrogen	N ₂	1-5
Helium	He	<0.5

Natural gas is generally considered to be of biogenic origin and is the result of the decay of animal remains and plant remains (organic debris) that has occurred over millions of years. Over time, the mud and soil that covered the organic debris changed to rock and trapped the debris beneath the newly-formed rock sediments. Pressure and, to some extent, heat (as yet undefined) changed some of the organic material into coal, some into crude oil, and some into natural gas. Whether or not the debris formed coal, crude oil, or gas depended upon the nature of the debris and the localized conditions under which the changes occurred.

Natural gas is found in reservoirs beneath the surface of the earth and is often associated with crude oil, although gas that is not associated with crude oil is also known. Production companies search for evidence of these reservoirs by using up-to-date technology that helps to determine the location of the gas and drill wells in the earth where it is likely to be found. Once brought from underground, the natural gas is refined to remove impurities like water, other gases, sand, and other compounds. Some hydrocarbon derivatives are removed and sold separately, including propane and butane. Other impurities are also removed, like hydrogen sulfide (the refining of which can produce sulfur, which is then also sold separately). After refining, the clean natural gas is transmitted through a network of pipelines that deliver natural gas to its point of use. Two new, and possibly large sources of methane that can be expected to extend the availability of natural gas, are methane hydrates (also called gas hydrates) and coal bed methane. Their production technologies have only recently been developed, and these sources are now becoming economically competitive.

Methane-rich gases are also produced by the anaerobic decay of non-fossil organic material and are generally referred to as biogas. Sources of biogas include (i) swamps, which produce swamp gas, (ii) marshes, which produce marsh gas, (iii) landfills, which produce landfill gas, (iv) as well as sewage sludge and manure, which produce gas by way of anaerobic digesters, and (v) livestock methane, which is produced by enteric fermentation in cattle.

Natural gas is a vital component of the supply of energy of the world, and it is one of the cleanest, safest, and most useful of all energy sources. However, it needs to be understood that the word gas has a variety of different uses, and meanings. Fuel for automobiles is also called gas (being a shortened version of gasoline), but that is a totally different fuel. The gas used in a barbecue grill is actually propane (C₃H₈), which, while associated with and commonly found in natural gas and crude oil, is not really natural gas.

Natural gas is the flammable gaseous mixture that occurs alone or with crude oil in reservoirs and is predominantly methane (CH₄) and some of the higher-molecular-weight higher paraffins (C_nH_{2n+2}) generally containing up to five carbon atoms (Table N-2). Non-flammable non-hydrocarbon components such as carbon dioxide (CO₂), hydrogen sulfide (H₂S), nitrogen (N₂), and helium (He) are often also present in natural gas. Carbon dioxide, nitrogen, and helium detract slightly from the heating value of natural gas. However, they are valuable and in certain natural gases where their concentrations are relatively high, they may be extracted commercially. In its purest form, as delivered to the consumer, natural gas is almost pure methane and the remaining hydrocarbon derivatives and non-hydrocarbon derivatives have been removed through refining.

Natural gas is colorless, shapeless, and odorless in its pure form. Quite uninteresting – except that natural gas is combustible, and when burned, it gives off a great deal of energy. Unlike other fossil fuels, however, natural gas is clean burning and emits lower levels of potentially harmful by-products into the air. It is the environmental aspect of gas use that is currently elevating the use of natural gas as an energy source of high importance.

There are several general definitions that have been applied to natural gas science and technology. For example, lean gas is gas in which methane is the major constituent. On the other hand, wet gas contains considerable amounts of the higher-molecular-weight hydrocarbon derivatives. To further define the terms dry and wet in quantitative measures, the term dry natural gas indicates that there is less than 0.1 gallon (1 gallon, US, = 264.2 m³) of gasoline vapor (higher-molecular-weight paraffins) per 1,000 ft³ (1 ft³ = 0.028 m³). The term wet natural gas indicates that there are such paraffins present in the gas, in fact more than 0.1 gal/1,000 ft³. Natural gas is considered dry when it is almost pure methane, having had most of the other commonly associated hydrocarbon derivatives removed. When other hydrocarbon derivatives are present, the natural gas is wet.

Sour gas contains hydrogen sulfide, whereas sweet gas contains little, if any, hydrogen sulfide. Residue gas is natural gas from which the higher-molecular-weight hydrocarbon derivatives have been extracted, and casing head gas is derived from crude oil but is separated at the separation facility at the well-head.

Natural gas is considered as an environmentally friendly clean fuel, offering important environmental benefits when compared to other fossil fuels. The superior environmental qualities over coal or crude oil are that emissions of sulfur dioxide are negligible or that the level of nitrous oxide and carbon dioxide emissions is lower. This helps to reduce problems of acid rain, ozone layer, or greenhouse gases. Natural gas is also a very safe source of energy when transported, stored, and used.

Neem Oil

Neem oil is a vegetable oil pressed from the fruits and seeds of neem (*Azadirachta indica*), an evergreen tree which is endemic to the India and has been introduced to many other areas in the tropics. It is perhaps the most important of the commercially available products of neem for organic farming and medicines.

Neem oil is generally light to dark brown, bitter, and has a rather strong odor that is said to combine the odors of peanut and garlic. It comprises mainly triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. It is hydrophobic in nature, and in order to emulsify it in water for application purposes, it must be formulated with appropriate surfactants.

Neem oil also contains steroids (campesterol, beta-sitosterol, stigmasterol) and a variety of triterpenoids of which azadirachtin is the most well-known.

While it has not yet been produced on a commercial scale, neem oil is being considered for biodiesel. The methyl esters of pongamia, Jatropha, and neem are derived through transesterification process, and these methyl esters (biodiesels) can be directly used in diesel engines without any engine modifications.

See also: Biodiesel, Transesterification, Vegetable Oil.

Neutralization Number

Neutralization is a process for reducing the acidity or alkalinity of a waste stream by mixing acids and bases to produce a neutral solution – also known as pH adjustment. The neutralization number is a measure of the acid or alkaline content of new oils and an indicator of the degree of oxidation degradation of used oils and, therefore, a number that indicates the degree of acidity or alkalinity of a substance determined by finding the amount of alkali or acid.

More specifically, thus, the neutralization number is the weight, in milligrams, of potassium hydroxide needed to neutralize the acid in 1 g of oil, which is an indication of the acidity of an oil.

See also: Acidity and Alkalinity, Acid Number.

Neutron

The neutron is a subatomic particle (symbol n or n^0 , which has a neutral (not positive or negative) charge and a mass slightly greater than that of a proton. Along with protons, neutrons constitute the nuclei of atoms. Since protons and neutrons behave similarly within the nucleus, and each has a mass of approximately one atomic mass unit, they are both referred to as nucleons.

The chemical properties of an atom are mostly determined by the configuration of electrons that orbit the nucleus of the atom nucleus. In addition, the electron configuration is determined by the charge of the nucleus, which is determined by the number of protons, or atomic number. The number of neutrons is the neutron number, and the neutrons do not affect the electron configuration, but the sum of atomic and neutron numbers is the mass of the nucleus and the isotopes of a chemical element differ only in neutron number. Neutrons are produced copiously in nuclear fission and in nuclear fusion.

See also: Electron, Neutron Moderator, Nuclear Fission, Nuclear Fusion, Proton.

Neutron Moderator

A neutron moderator is a medium that reduces the speed of fast neutrons without (in theory) without capturing any of the neutrons, thereby leaving them as thermal neutrons with only minimal thermal (kinetic) energy. These thermal neutrons are more susceptible than fast neutrons to propagate a nuclear chain reaction of uranium-235 (^{235}U) or another fissile isotope by colliding with the atomic nuclear.

Thus, the function of the moderator is to slow down the fast neutrons and the atoms of the moderator material need to have a size close to neutrons. These materials should have low neutron absorption cross section and can also act as a coolant requiring high thermal conductivity and heat capacity to absorb the heat. The primary function of a coolant is to transfer heat generated at the nuclear reactor core.

Light water is the most commonly used moderator, although the term is slightly ambiguous, usually meaning natural fresh water but typically refers to deuterium-depleted water. Solid graphite and heavy water (D_2O , $^2\text{H}_2\text{O}$) are the main alternatives for neutron moderators. Beryllium has also been used as a neutron moderator, and hydrocarbon derivatives have been suggested as another possibility.

The main benefit of using a moderator in a nuclear explosive is that the amount of fissile material needed to reach the critical stage may be greatly reduced. Slowing of fast neutrons will increase the cross section of the neutron absorption, thereby reducing the critical mass. However, there is a side effect – as the chain reaction progresses, the moderator will be heated, thus losing its ability to cool the neutrons. Another effect of moderation is that the time between subsequent neutron generations is increased, slowing down the reaction. This makes the containment of the explosion a problem; the inertia that is used to confine implosion-type bombs will not be able to confine the reaction. The end result may be a lower reaction climax rather than a prominent explosion.

See also: Nuclear Energy, Nuclear Fission, Nuclear Reactor.

Nitrogen Cycle

The nitrogen cycle is complex, involving the conversion of atmospheric nitrogen (N_2) to ammonia (NH_3) and nitrate (NO_3) derivatives through different mechanisms. While nitrogen in the soil can increase agricultural yields, excess reactive nitrogen is responsible for many environmental problems, including acidification, smog formation, eutrophication/hypoxia (a condition in which the body or a region of the body is deprived of adequate oxygen supply), and global warming potential in the form of nitrous oxide (N_2O). Also, nutrient runoff from fertilized soybean fields provokes eutrophication which is an accumulation of nutrients in water that prompts algal blooms. Organisms in the affected aquatic environment will die and decay, creating a high oxygen demand. Extreme cases of eutrophication create hypoxia and drive oxygen levels so low that the ecosystem is no longer capable of supporting life.

See also: Biogeochemical Cycles.

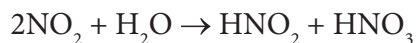
Nitrogen Oxides

Nitrogen oxides (NO_x) are produced during combustion; precursors to acid deposition (acid rain). NO_x is a generic term for mono-nitrogen oxides (NO and NO_2). These oxides are produced during combustion. At ambient temperatures, the oxygen and nitrogen gases in air will not react with each other.

In the presence of excess oxygen (O_2), nitric oxide (NO) will be converted to nitrogen dioxide (NO_2).

When NO_x and volatile organic compounds (VOCs) react in the presence of sunlight, they form photochemical *smog*, a significant form of air pollution, especially in the summer.

Mono-nitrogen oxides eventually form nitric acid when dissolved in atmospheric moisture, forming a component of acid rain:



Nitric oxide will oxidize to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid:



Mono-nitrogen oxides are also involved in production of ozone in the troposphere.

Nitrogen Oxides Control

Nitrogen oxides are produced in the combustion of fuels; nitrogen oxides (NOX) control can be approached in two ways: by adjusting combustion conditions to minimize nitrogen oxides production, or by cleaning the nitrogen oxides that are produced from the stack gases. Combustor conditions can be designed for low NOX production, and gas cleaning systems can also be added in the future if the need arises for further control of nitrogen oxides.

See also: Gas Cleaning.

Noise Control

Preparation plants for the production of feedstocks invariably contain various types of active machinery, in addition to large throughput tonnage of free-falling solids, and have long been recognized as presenting a serious noise problem. Most of the noise control measures may be classified broadly into measures that (1) suppress noise formation or (2) provide noise containment. Examples of the former include the installation of mufflers on air pumps and of rubber screen cloths and resilient screen decks and chute liners. Noise containment requires erection of barriers, either walls or curtains.

Non-Hydrocarbon Components

Crude oil which contains only hydrocarbon derivatives is, in fact, an extremely complex mixture. The phenomenal increase in the number of possible isomers for the higher hydrocarbon derivatives makes it difficult, if not impossible in most cases, to isolate individual members of any one series having more than, say, 12 carbon atoms.

Inclusion of organic compounds of nitrogen, oxygen, and sulfur serves only to present crude oil as an even more complex mixture than was originally conceived. Nevertheless, considerable progress has been made in the isolation and/or identification of the lower- molecular-weight hydrocarbon derivatives, as well as accurate estimations of the overall proportions of the hydrocarbon types present in crude oil. Indeed, it has been established that, as the boiling

point of the crude oil fraction increases, not only the number of the constituents but the molecular complexity of the constituents also increases.

Crude oils contain appreciable amounts of organic non-hydrocarbon constituents, mainly sulfur-, nitrogen-, and oxygen-containing compounds and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the higher-boiling fractions and in the non-volatile residues.

Although their concentration in certain fractions may be quite small, their influence is important. For example, the decomposition of inorganic salts suspended in the crude can cause serious breakdowns in refinery operations; the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. The presence of organic acid components, such as mercaptans and acids, can also promote metallic corrosion. In catalytic operations, passivation and/or poisoning of the catalyst can be caused by deposition of traces of metals (vanadium and nickel) or by chemisorption of nitrogen-containing compounds on the catalyst, thus necessitating the frequent regeneration of the catalyst or its expensive replacement.

The presence of traces of non-hydrocarbon derivatives may impart objectionable characteristics in finished products, such as discoloration, lack of stability on storage, or a reduction in the effectiveness of organic lead antiknock additives. It is thus obvious that a more extensive knowledge of these compounds and of their characteristics could result in improved refining methods and even in finished products of better quality. The non-hydrocarbon compounds, particularly the porphyrins and related compounds, are also of fundamental interest in the elucidation of the origin and nature of crude oils. Furthermore, knowledge of their surface-active characteristics is of help in understanding problems related to the migration of oil from the source rocks to the actual reservoirs.

Non-Methane Hydrocarbons

Non-methane hydrocarbons (Table N-3) are the organic compounds of carbon and hydrogen that are not straight chain, saturated (no more hydrogen can be added) molecules in which the carbon atoms are joined to each other by single bonds.

Table N-3 Simple non-methane hydrocarbons.

Number of carbon atoms	Alkane	Alkene	Alkyne	Cycloalkane	Alkadiene
2	Ethane	Ethylene	Acetylene		
3	Propane	Propylene	Propyne	Cyclopropane	
4	Butane, iso-Butane	Butene	Butyne	Cyclobutane	Butadiene
5	Pentane, iso-Pentane, Neopentane	Pentene	Pentyne	Cyclopentane	Pentadiene
6	Hexane	Hexene	Hexyne	Cyclohexane Methylcyclopentane Ethylcyclobutane Propylcyclopropane	Hexadiene
7	Heptane	Heptene	Heptyne	Cycloheptane Methylcyclohexane	Heptadiene
8	Octane	Octene	Octyne	Cyclooctane	Octadiene
9	Nonane	Nonene	Nonyne	Cyclononane	Nonadiene
10	Decane	Decene	Decyne	Cyclodecane	Decadiene

Because of differences in molecular structure, the empirical formula remains different between hydrocarbons; in linear, or straight-chain alkanes, alkenes and alkynes, the amount of bonded hydrogen lessens in alkenes, and alkynes due to the self-bonding or catenation of carbon preventing entire saturation of the hydrocarbon by the formation of double or triple bonds.

In simple chemistry, as per valence bond theory, the carbon atom must follow the 4-hydrogen rule which states that the maximum number of atoms available to bond with carbon is equal to the number of electrons that are attracted into the outer shell of carbon. In terms of shells, carbon consists of an incomplete outer shell, which comprises 4 electrons, and thus has 4 electrons available for covalent or dative bonding.

See also: Alkanes.

Non-Conventional Fuel Sources

Non-conventional fuel sources are sources of fuels (alternate or synthetic fuels) other than traditional crude oil. Three types of non-conventional oil reserves can be discerned: heavy crude oil, extra heavy crude oil, and tar sand bitumen. Medium heavy crude oil and extra heavy crude oil are mobile at reservoir conditions but are typically immobile at ambient temperature, but the highly viscous tar sand bitumen is immobile at deposit (reservoir) conditions.

Gaseous, liquid, or solid synthetic fuels are obtained by converting a carbonaceous material to another form. The most abundant naturally occurring materials suitable for this purpose are (i) tar sand bitumen, (ii) extra heavy crude oil, (iii) coal, and (iv) oil shale. The conversion of these raw materials to synthetic fuels can replace depleted, unavailable, or costly supplies of natural fuels.

Biomass is another carbonaceous material that can also be converted to synthetic fuels – such as the fermentation of grain to produce alcohol, which is the best-known example. Wood is also an abundant and accessible source of bio-energy, and the procedures for the gasification of cellulosic materials have much in common with the conversion of coal to gas.

Currently, non-conventional oil production is less efficient and some types have a larger environmental impact relative to conventional oil production. Non-conventional types of production include tar sand, extra heavy crude oil, coal, oil shale, and biofuels as well as liquid fuels from natural gas through processes such as the Fischer-Tropsch process. These non-conventional sources of oil may be increasingly relied upon as fuel for transportation as the price of conventional crude oil increases and supplies dwindle.

However, conventional sources of liquid fuels from crude oil are currently preferred because they provide a much higher ratio of extracted energy over energy used in extraction and refining processes. Technology, such as using steam injection in heavy crude oil reservoirs, continues to serve as a means of extracting heavy crude oil, while mining serves as the only commercial production of tar sand bitumen.

See also: Bitumen Coal, Crude Oil.

NO_x

NO_x refers to the oxides of nitrogen that are produced during combustion or nitrogen-containing fuels or, under certain circumstances, when air is used as the source of oxygen. Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air. The formation rate is primarily a function of temperature and the residence time of nitrogen at that temperature. At high temperatures, usually above 1,600°C (2,900°F), molecular nitrogen (N₂) and oxygen (O₂) in the combustion air disassociate into their atomic states and participate in a series of reactions forming a variety of nitrogen oxides.

In fact, the term NO_x or nitrogen oxides typically refers to any binary compound of oxygen and nitrogen, or to a mixture of such compounds:

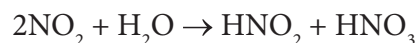
- Nitric oxide (NO), nitrogen(II) oxide.
- Nitrogen dioxide (NO₂), nitrogen(IV) oxide.
- Nitrous oxide (N₂O), nitrogen(I) oxide.
- Dinitrogen trioxide (N₂O₃), nitrogen(II, IV) oxide.

Dinitrogen tetroxide (N_2O_4), nitrogen(IV) oxide.

Dinitrogen pentoxide (N_2O_5), nitrogen(V) oxide.

The last three compounds are unstable but may be formed during the combustion process before decomposing to more stable forms of nitrogen oxide.

Mono-nitrogen oxides eventually form nitric acid when dissolved in atmospheric moisture, forming a component of acid rain:



Technologies such as flameless oxidation (FLOX) and staged combustion significantly reduce thermal NOx in industrial processes. Water Injection technology, whereby water is introduced into the combustion chamber, is also becoming an important means of NOx reduction through increased efficiency in the overall combustion process. Alternatively, the water (e.g., 10 to 50%) is emulsified into the fuel oil prior to the injection and combustion. This emulsification can either be made in-line (unstabilized) just before the injection or as a drop-in fuel with chemical additives for long-term emulsion stability (stabilized). Other technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), reduce post combustion NOx.

Nuclear Energy

Nuclear energy is energy that can be released from the nucleus of an atom. There are two ways to produce this energy, either by fission or fusion. Fission occurs when the atomic nucleus is split apart. Fusion is the result of combining two or more light nuclei into one heavier nucleus.

Atoms are made up of several parts: protons, neutrons, electrons, and a nucleus. A nucleus is the positively charged center of an atom. Protons are positively charged particles, and neutrons are uncharged particles. Electrons orbit around the nucleus and are negatively charged. Fission can occur in two ways—first, in some very heavy elements, such as rutherfordium, the nucleus of an atom can split apart into smaller pieces spontaneously.

With lighter (lower atomic weight) elements, it is possible to hit the nucleus with a free neutron, which will also cause the nucleus to break apart, and a significant amount of energy is released when the nucleus splits. The energy released takes two forms: light energy and heat energy. Radioactivity is also produced. Atomic bombs let this energy out all at once, creating an explosion. Nuclear reactors let this energy out slowly in a continuous chain reaction to make electricity. After the nucleus splits, new lighter atoms are formed. More free neutrons are thrown off that can split other atoms, continuing to produce nuclear energy.

Nuclear energy can be used for various industrial applications, such as seawater desalination, hydrogen production, district heating or cooling, the extraction of tertiary oil resources, and process heat applications such as cogeneration, coal-to-liquids conversion, and assistance in the synthesis of chemical feedstock. A large demand for nuclear energy for industrial applications is expected to grow rapidly on account of steadily increasing energy consumption, the finite availability of fossil fuels, and the increased sensitivity to the environmental impacts of fossil fuel combustion. With increasing prices for conventional oil, unconventional oil resources are increasingly utilized to meet such growing demand, especially for transport.

Nuclear binding energy is the energy required to split a nucleus of an atom into the component parts. The term nuclear binding energy may also refer to the energy balance in processes in which the nucleus splits into fragments composed of more than one nucleon. If new binding energy is available when light nuclei fuse, or when heavy nuclei split, either of these processes result in releases of the binding energy. This energy, available as *nuclear energy*, can be used to produce electricity (nuclear power) or as a nuclear weapon.

An absorption or release of nuclear energy occurs in nuclear reactions of radioactive decay. Those reactions that absorb energy are called endothermic reactions, and those that release energy are exothermic reactions. Energy is consumed or liberated because of differences in the nuclear binding energy between the incoming and outgoing products of the nuclear transmutation.

Thus, nuclear energy or nuclear power is the use of exothermic nuclear process of nuclear binding energy to generate useful heat and electricity. The term includes nuclear fission, nuclear decay, and nuclear fusion. Presently, the nuclear fission of elements in the actinide series of the Periodic Table of the Elements produce the vast majority of nuclear energy in the direct service of humankind, with nuclear decay processes, primarily in the form of geothermal energy, and radioisotope thermoelectric generators, in niche uses making up the remainder.

Nuclear energy offers a low carbon alternative and has important potential advantages over other sources being considered for future energy. There are no technological impediments to extracting heat and steam from a nuclear power plant. This has been proven for low temperatures (<200°C) with nuclear assisted district heating and desalination with an experience of approximately 750 reactor operation years from around 70 nuclear power plants. Detailed site-specific analyses are essential for determining the best energy option. The development of small- and medium-sized reactors would therefore be better suited for cogeneration and would facilitate non-electric applications of nuclear energy. The possibility of large-scale distribution systems for heat, steam, and electricity supplied from a central nuclear heat source (such as a multiproduct energy center) could attract and serve different kinds of consumers concentrated in industrial parks.

Nuclear energy is energy in the core of an atom which is made up of three particles – protons, neutrons, and electrons. Protons carry a positive electrical charge, and electrons carry a negative electrical charge. Neutrons do not have an electrical charge. The energy is located in the bonds that hold the nucleus together. This nuclear energy can be released when those bonds are broken. The bonds can be broken through nuclear fission, and this energy can be used to produce (generate) electricity.

The main interest in this source of energy is physically based on the so-called energy mega-factor. When comparing the energy released by a chemical reaction, as in the combustion phase of a coal (C) atom or a methane (CH₄) molecule, with a nuclear reaction on a nucleus of uranium (²³⁵U isotope) by a neutron (n), the amount of energy (Q, in electron volts) differs from six orders of magnitude:



In this equation, F1 and F2 are fission fragments.

Thus, in terms of energy release, 1 unit weight of nuclear fuel (UO₂) is energetically equivalent to 128 thousand units (by weight) of wood, or 70 thousand units (by weight) of crude oil, or 80 thousand (by weight) of coal with no emissions of carbon dioxide. However, there are other hazards to the use of nuclear energy that must be addressed as part of the planning process. These include the disposal of spent nuclear fuel as well as the potential for a nuclear meltdown.

Energy from nuclear sources may be the result of nuclear fission, which uses uranium ore or refined uranium-235 (²³⁵U) as its basic energy source. In nuclear fission, atoms are split apart (hence the term fissile material as applied to the source) which releases energy. All nuclear power plants use nuclear fission, and most nuclear power plants use uranium atoms. During nuclear fission, a neutron collides with a uranium atom and splits it, releasing a large amount of energy in the form of heat and radiation. More neutrons are also released when a uranium atom splits. These neutrons continue to collide with other uranium atoms, and the process repeats itself over and over again. This process is called a nuclear chain reaction. This reaction is controlled in nuclear power plant reactors to produce a desired amount of heat.

For this type of energy, the ore must be concentrated into fissionable isotopes through nuclear processing. Eventually, the spent material must be replaced, and the resources of uranium ore may be limited as determined by a specific test (ASTM E901). Hence, the need to explore the potential for generating more of the fissionable isotopes.

However, the use of such materials has become the core of a major controversy which threatens to be, at least for the time being, the death-knell of the nuclear industry.

Nuclear fusion, unlike nuclear fission which involves the use of fissionable material, involves the fusion of hydrogen nuclei. The concept has been suggested as having the potential to provide a clean and virtually unlimited supply of energy. However, it is generally felt that the technology is at the stage where several decades appear to be needed for the performance of believable laboratory-scale experiments which are critical to the development of controlled energy from fusion.

In nuclear fusion, the atoms are combined or fused together to form a larger atom. Fusion is the source of energy in the sun and stars. Developing technology to harness nuclear fusion as a source of energy for heat and electricity generation is the subject of ongoing research, but whether or not it will be a commercially viable technology is not yet clear because of the difficulty in controlling a fusion reaction.

Currently, at nuclear power plants, the heat to make the steam is created through nuclear fission which releases heat. In a nuclear power plant, uranium is the material used in the fission process and the heat from fission is used to create steam to turn a turbine which, in turn, produces electricity. However, nuclear energy can be as hazardous as any fossil fuel in terms of destruction of the environment, and deserves some comment insofar as an appreciation of its use may assist in the general background and aid in putting fossil fuel resources into a more complete context.

Nevertheless, as long as suitable safety regulations are applied, energy from nuclear sources has shown potential to be a significant energy source in the future. The technology is known but has suffered some setbacks. Accidents and dubious claims of the ease with which energy may be derived from nuclear sources have reduced the credibility of the nuclear industry. Nevertheless, the potential still exists for the extraction of energy from nuclear sources.

Hence, the continued use of the so-called conventional fuel resources is derived from the remains of ancient plants and animals. Those same resources which have been instrumental in the phenomenal expansion of the industrialized world. And also, those same resources which can have serious adverse effects on the flora and fauna (including man) of the world.

Nuclear Energy – Environmental Impact

The chief benefit to the environment of nuclear power plants is that they do not emit (give off) harmful gases, such as carbon dioxide and sulfur dioxide. In this way, nuclear power plants differ from conventional (natural gas-fired, crude oil-fired, coal-fired) power plants, which emit these gases primarily because they burn coal, a fossil fuel. If the energy generated by nuclear power plants worldwide were instead generated by burning coal, the amount of additional carbon dioxide released into the atmosphere would be approximately 1,600 million tons. Moreover, burning coal releases toxic heavy metals, including arsenic, cadmium, lead, and mercury.

By not emitting these gases, nuclear energy does not contribute to environmental problems such as air pollution, smog, and the greenhouse effect, which refers to the ability of some gases (such as carbon dioxide) to accumulate in the air, thereby trapping the heat from the Sun which causes an increase in average temperatures around the world – often referred to as global warming which is blamed for the melting of the polar ice, raising sea levels and endangering coastal cities. Furthermore, by not emitting pollutants (such as nitrogen oxides and sulfur oxides), nuclear power plants do not contribute to acid rain. Acid rain is any form of precipitation that is more acidic than normal because the water has absorbed acidic pollutants from the air. Acid rain can harm crops and forests. It can also contribute to the deterioration of buildings and public monuments, which dissolve because of the acid in precipitation.

Nuclear power plants also do not harm surrounding bodies of water. A myth that some people believe is that nuclear plants discharge water into nearby lakes and streams that is either radioactive or extremely hot. This is not true. The water released from a nuclear plant never comes into contact with the radiation. Further, if the water is too hot to be discharged, it is cooled either in a cooling pond or in cooling towers before release.

However, nuclear power plants have a low impact on the environment, especially when compared to hydroelectric dams. While such dams have the benefit of not emitting harmful gases or pollutants, the dams have a major impact on the surrounding environment. By turning rivers into huge lakes, they disrupt vegetation and wildlife. Many dams have displaced (driven out) large numbers of people. Further, the reservoirs behind hydroelectric dams emit their own form of pollution. As the water level of the reservoir falls, the wet ground that surrounds it supports the growth

of vegetation. As the water rises, this vegetation is covered and rots. The rotting vegetation emits methane gas, a pollutant. In addition, hydroelectric dams have an adverse effect on fish because they disrupt breeding and spawning grounds.

Nuclear power plants do not have harmful effects on wildlife. In fact, they often can have beneficial effects. For example, when cooled water is released from the plant, the water often contributes to the formation of wetlands. These wetlands can become nesting grounds and provide habitat for birds, fish, and other animals. Some companies that build and run nuclear plants even develop wildlife preserves and parks in the surrounding area, where plants grow abundantly in the moist soil.

See also: Acid Rain.

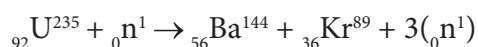
Nuclear Fission

An atom is made up of three kinds of particles: neutrons, protons, and electrons. Two of these particles, neutrons and protons, are found in the nucleus, or center, of an atom. A neutron does not have an electrical charge. It is called a neutron because its electrical charge is neutral. A proton has a positive electrical charge. Circling around the nucleus of an atom in layers are electrons, which have a negative electrical charge. To keep the overall electrical charge neutral, an atom has to have the same number of protons and electrons. Positive and negative electrical charges attract each other. The charges bind the particles of an atom together. When an atom is split, some of this energy is released.

When a nucleus undergoes fission, a considerable amount of energy is released. The energy carried by the neutrons represents a small fraction of the total energy released. Most of this energy is carried by the fission products in the form of kinetic energy. Expelled at a velocity of in excess of 8,000 kilometers (5,000 miles) per second, these fission products push their way through the other atoms by knocking against them. During these collisions, they rapidly lose their speed (and thus energy) by heating up the surrounding environment, before stopping in the bulk of the uranium. Their initial energy is finally transformed into heat, and the local temperature in the uranium increases. In a nuclear reactor, this heat is recovered to generate electricity.

By far the most important element for nuclear fission is uranium-235 (^{235}U or U-235), and it is the principal constituent of the fuel rods in a nuclear reactor. In a fission reaction, besides the two fission products, several neutrons (in the case of U-235, typically two to three) are emitted.

For example, in 235 grams of U-235, there are as many as 6×10^{23} atoms (the Avogadro number) and all of these atoms can undergo fission. Thus:



In this fission event, one among billion quadrillion identical ones, the fissionable uranium atom (nucleus) reacts with a neutron, becomes temporarily unstable, and is fragmented very soon thereafter into a nucleus of barium (Ba) and a nucleus of krypton (Kr). Also, the number of protons on the left-hand side of a nuclear equation (in this case, $92 + 0 = 92$) is equal to the number of protons on the right-hand side ($56 + 36 = 92$); the number of neutrons is also equal on both sides of the equation ($235 + 1 = 144 + 89 + 3$). Atoms are not conserved, but nucleons are. This is the difference between a chemical reaction and a nuclear reaction. Also, atoms are conserved in chemical reactions; they are just rearranged to form different molecules. In nuclear reactions, nucleons are rearranged to form different nuclei but they are conserved.

Nuclear fission is an example of a chain reaction in which each one of the three neutrons produced in the first fission event goes on to collide with other U-235 nuclei. This new collision event will in turn produce three additional neutrons; so after two collisions, a total of nine neutrons will be obtained. This increase in neutron inventory (3-9-27-81-243-729-et seq) is similar to the population rise and is an example of exponential growth. Because this exponential growth is accompanied by heat release, an exponential buildup of heat occurs at the same time. There is no way to dissipate or carry away all this heat, so the temperature of the solid material (within which fission occurs) increases; the material melts and then vaporizes. This in turn causes a pressure buildup which ultimately results in an explosion, just like in an overinflated balloon.

Thus, the principle of chain reaction involves bombardment of the uranium-235 nucleus neutrons, upon which fission occurs at a high probability. The neutrons produced in this process can cause more fissions, and, consequently, the process becomes self-sustaining and no external neutron source is needed any longer. If the neutrons produced from a fission induce only one new fission (because of escaping from the system or being captured inside), we say that the chain reaction is of constant intensity. If the neutrons generated from a fission reaction induce more than one fission, then more and more fission reactions will take place in a unit time and the chain reaction will be diverging.

As much as 85% of the energy released in the fission process appears as kinetic energy of the fragments. As the high-speed fragments collide with surrounding matter, they induce random motion of the surrounding atoms and molecules; their kinetic energy is thus converted to heat. This heat is used in turn to produce electricity in a nuclear reactor or is allowed to cause an explosion in an atomic bomb. The fate of the neutrons produced in the fission process is the key to understanding the difference between a controlled nuclear reaction, which takes place inside a nuclear reactor, and an uncontrolled nuclear reaction, which leads to the explosion of an atomic bomb.

The probability that a high energy neutron emitted in a fission reaction can directly cause fission is quite low. In order to build a system in which fast neutrons sustain the chain reaction, very highly enriched uranium is needed. A more easily feasible way is to use materials that slow the neutrons down to such low energies at which the probability of causing a fission is significantly higher. These neutrons slowing down materials are the so-called moderators. With the aid of some adequate moderator, one might as well achieve chain reaction using natural (0.7% U-235 content) uranium.

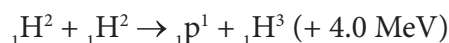
Typically, at the fission of uranium-235, two to three neutrons are released, but not all of these cause fission. The neutronic state can be characterized by the so-called multiplication factor (k), which is the ratio of the number of neutrons in a neutron generation and the number of neutrons in the preceding generation. The neutron generation is the time that elapses between the birth of a neutron and the birth of neutrons from the subsequent fission which is caused by the given neutron and is on the order of 10^{-9} second (i.e., 1 nanosecond) for pure uranium-235. The number of neutrons present in the reactor must be regulated or controlled since this determines the rate of fission and thus the energy released per second. In order to control the chain reaction, one should use materials which tend to capture neutrons at a high probability. The most widespread neutron absorbers are cadmium (Cd) and boron (B).

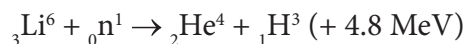
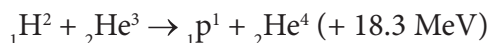
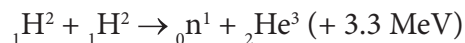
The so-called control rods are important tools of control and can be found in every reactor. These are made of neutron-absorbing materials and can be moved between the fuel assemblies. For example, if one wishes to decrease the power of the reactor, it is sufficient to push in a control rod a little further. The control rods are particularly useful for short-term control and stopping the reactor. For long-term regulation, usually boric acid dissolved in the coolant is used.

Nuclear Fusion

The nuclear fusion process is the opposite of the fission process and involves the combination of light (low density, low atomic number) nuclei in order to release excess binding energy, and they form a heavier nucleus. Fusion reactions are responsible for the energy of the sun. They have also been used on earth for uncontrolled release of large quantities of energy in the thermonuclear or hydrogen bombs. However, the enormous potential and the problems associated with controlled use of this essentially nondepletable energy source need side-by-side consideration.

The concept of nuclear fusion occurs when the nuclei of two light atoms are brought closer to each other, they become increasingly destabilized, due to the electric repulsion of their positive charges. Work must be expended to achieve this, and so the energy of the two nuclei increases. If this activation energy is provided to overcome the repulsive forces, fusion of the two nuclei into a stable heavier nucleus will take place and a large amount of energy will be released. The net energy output is potentially larger in the case of fusion than in the case of fission. For example, the fusion of deuterium (shown as H^2) and tritium (shown as H^3) into helium (He) is only one of the possible reactions that could be the basis for the fusion power reactors of the future. Thus:





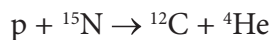
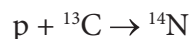
In this equation, *p* signifies a proton, *n* signifies a neutron, and *Li* is lithium.

Deuterium and tritium are the main ingredients in most fusion reactions. Deuterium is a stable form of hydrogen; it does occur (as trace amounts) in ordinary water. Tritium is a radioactive form of hydrogen that does not occur in nature. In contrast to the situation with fission, where tritium is produced (and thus contributes to radioactivity), here it is consumed. As shown above, it can be obtained from lithium, Li-6, a relatively abundant metal found in mineral ores. A simple calculation, based on the fact that there is one deuterium atom in every 6,500 atoms of hydrogen, shows that in 65,000 pounds of water, there is approximately one pound of deuterium.

The reaction between deuterium (H^2) and tritium (H^3) has the fast reaction rate and requires the lowest temperature of all the fusion reactions, so it is the first choice for a fusion power plant. Adequate sources of deuterium and tritium are thus important, independent of what type of confinement system, magnetic or inertial, is employed.

One gram of deuterium will produce 300 GJ of electricity, and providing for all of the world's present-day energy consumption (equivalent to approximately 3×10^{11} GJ per year) would require approximately 1,000 tons of deuterium a year. The source of deuterium is straightforward because approximately 1 part in 6,700 of water is deuterium, and 1 gallon of water used as a source of fusion fuel could produce as much energy as 300 gallons of gasoline. When all the water in the oceans is considered, this amounts to over 10^{15} tons of deuterium – enough to supply our energy requirements indefinitely. Extracting deuterium from water is straightforward using electrolysis, and the cost of the fuel would be negligible compared to the other costs of making electricity. Since water is an abundant resource on the Earth, and the fact, together with the fact that enormous amounts of energy are released in fusion reactions, makes fusion an essentially nondepletable energy source.

A second series of nuclear reactions can convert hydrogen into helium, and it is now thought that it is the dominant process in stars that are hotter and more massive than the Sun. The reaction sequence is as follows:



In the first stage, a proton reacts with a ${}^{12}\text{C}$ nucleus to form nitrogen ${}^{13}\text{N}$, which is unstable and decays to ${}^{13}\text{C}$. Further stages build up through ${}^{14}\text{N}$ and ${}^{15}\text{O}$ to ${}^{15}\text{N}$, which then reacts with a proton to form ${}^{12}\text{C}$ and ${}^4\text{He}$. At the end of the sequence, the ${}^{12}\text{C}$ has been recycled and can start another chain of reactions, so it acts as a catalyst. Overall, four protons have been replaced with a single helium nucleus, so the energy release is the same as for the proton cycle.

Fusion offers several advantages over fission such as (i) the reserves of fusible isotopes are much larger than those of fissionable isotopes and (ii) the products of fusion reactions are less radioactive than the products of fission reactions. Among the products of the fusion reactions listed above, only tritium and the neutrons are radioactive. In addition, fusion is inherently safe. Insofar as there would be little fusible material at any given time in the reactor, and the likelihood of a runaway reaction would thus be small and perhaps even unlikely.

The basic challenges of fusion are the following: (i) heating of the reacting mixture to a high temperature, to overcome the repulsive forces of positively charged nuclei, (ii) compressing the mixture to a high density so that the probability of collision and, thus, reaction among the nuclei can be high, and (iii) keeping the reacting mixture together long enough for the fusion reaction to produce energy at a rate that is greater than the rate of energy input (as heat and compression).

The first challenge is that of providing a huge amount of energy to the reactants – fusion is a thermonuclear reaction. The second and third challenges are collectively referred to as the confinement problem. It is easily understood that the reacting mixture – called ‘plasma’ at the high temperatures involved – cannot be brought together (or confined) in ordinary vessels. The presence of solid vessels is ruled out because they would carry away the heat necessary to reach the high ignition temperatures. Magnets (magnetic confinement) and lasers (inertial confinement) are used instead.

See also: Electrolysis.

Nuclear Power

Nuclear power is the power derived from the fission or fusion of atomic species. The primary use of nuclear power is the large-scale generation of base load electricity by the fission (i.e., splitting) of the uranium isotope (^{235}U). At present, there is still public concern related to the use of nuclear power. However, a more careful analysis shows that this form of energy is considerably more desirable than is currently perceived and will likely be one of the main practical solutions for the future production of CO_2 free electricity.

There are several comparisons with fossil fuel plants that show why nuclear power has received so much attention as a source of electricity. The first involves the energy content of the fuel. A nuclear reaction produces on the order of one million times more energy per elementary particle than a fossil fuel chemical reaction. The implication is that much less nuclear fuel is required to produce a given amount of energy.

A second point of comparison is environmental impact. Nuclear power plants produce neither carbon dioxide nor other harmful emissions. This is a major environmental advantage. Another issue is safety. The worst accident in a USA plant occurred at Three Mile Island. This was a financial disaster for the power company but only a negligible amount of radiation was released to the environment. The reason is that Western nuclear power plants are designed with many overlapping layers of safety to provide “defense in depth” culminating with a huge, steel reinforced containment vessel around the reactor to protect the public in the case of a worst accident. The large loss of life and wide environmental damage resulting from the Chernobyl accident occurred because there was no containment vessel around the reactor.

A major issue is the extent of the reserves of nuclear fuels. In the simplest sense, it can be assumed that uranium-235 is the basic fuel and once most of it has been consumed in the reactor, the resulting spent fuel rods are buried in a permanent, non-retrievable repository. In this scenario, there is enough uranium-235 to provide electricity at the present rate for several hundred years. On the other hand, the spent fuel rods contain substantial amounts of plutonium which can be chemically extracted and then used as a new nuclear fuel. In fact, it is possible to use the resulting plutonium in such a way that it actually breeds more plutonium than is being consumed. The use of such “breeder” reactors extends the reserves of nuclear fuels to many thousands of years. Breeders are more expensive than conventional nuclear plants and are not currently used because of the ready availability of low-cost uranium-235. However, in the long term, breeders may be one of the energy sources of choice.

Nuclear waste and how to dispose of it is another important issue. Here too, there are subtleties. One point is that many of the radioactive fission by-products have reasonably short half-lives, on the order of 30 years or less. They need to be stored for approximately one hundred years during which time they self-destruct by radioactive decay into a harmless form, an ideal end result. It is the long-lived, multi-thousand year wastes that receive much public attention and scrutiny. Several possible solutions have received serious consideration. The waste can be dissolved in glass (i.e., vitrification) and permanently stored. The fuel can be chemically reprocessed for re-use in regular or breeder reactors, thereby transforming much of the long-lived waste into useful electricity. Third, there are techniques that, while currently expensive, transmute long-lived, non-fission radioactive waste by-products into harmless elements.

Also, a critical point is that the total volume of nuclear waste is small. The total nuclear “rubbish” resulting from powering Boston for one year would fill up only a small fraction of a pickup truck. The conclusion is that there are a variety of technological solutions to the waste disposal problem.

See als: Nuclear Energy, Nuclear Fission, Nuclear Fusion, Nuclear Power Plant, Nuclear Reactor.

Nuclear Power Plant

A nuclear power plant is a system in which some of the energy released by nuclear fission is used to generate electricity. Every such plant contains four fundamental elements: reactor, coolant system, electrical–power generating unit, and safety system. In the plant, heat is produced during nuclear fission to boil water into steam, which turns the blades of a steam turbine. As the turbine blades turn, they drive generators that make produce electricity.

The source of energy in a nuclear reactor is a fission reaction in which neutrons collide with nuclei of uranium-235 (^{235}U) or plutonium-239 (^{239}Pu) (the fuel), causing them to split apart. The products of a fission reaction include not only energy but also new elements (known as fission products) and free neutrons. A constant and reliable flow of neutrons is insured in the reactor by a moderator, which slows down the speed of neutrons, and by control rods, which limit the number of neutrons available in the reactor and, hence, the rate at which fission can occur. In a nuclear weapon, the fission chain reaction), once triggered, proceeds at an exponentially increasing rate, resulting in an explosion. In a nuclear reactor, the process proceeds at a steady, controlled rate. Most commercial nuclear power plants are incapable of undergoing an explosive nuclear chain reaction, even should their safety systems fail. However, this is not the case with all research reactors (such as some breeder reactors).

Energy produced in the reactor is carried away by means of a coolant such as pressurized water, liquid sodium, or carbon dioxide. The circulating coolant absorbs heat in the reactor; once outside the reactor, it is allowed to boil or the heat it contains is used to boil water in a secondary loop. Steam produced in either of these ways is then piped into the electrical generating unit, where it turns the blades of a turbine. The turbine, in turn, turns a generator that produces electrical energy.

Every nuclear plant is also required to have an elaborate safety system to protect against the most serious potential problem of all, loss of coolant. If such an accident were to occur, the reactor core might melt itself down, possibly breaching the structures which contain it and releasing radioactive materials to the rest of the plant and, perhaps, to the outside environment. To prevent such an accident, the pipes carrying the coolant to and from the reactor are required to be very thick and strong. In addition, backup supplies of the coolant must be available to replace losses in case of a leak. Another safety feature is a system of high-efficiency filters through which all air leaving the building must pass. These filters are designed to trap microscopic particles of radioactive materials that might otherwise be vented to the atmosphere. Other specialized devices and systems have also been developed for dealing with other kinds of accidents in various parts of the power plant.

Overall, a nuclear power plant can be considered to be similar to a conventional thermal power plant: Each type uses steam to drive a turbine generator that produces electricity. The heat energy of the steam is converted to mechanical energy in the turbine, and the generator then converts the mechanical energy into electrical energy, or electricity. Although the turbine functions equally well no matter where the steam comes from, the origin of the steam is important.

In terms of the production of steam, conventional plants burn natural gas, crude oil, or coal, and heat from the combustion of these fossil fuels boils water to make steam. In nuclear plants, on the other hand, no burning or combustion takes place and nuclear fission is used instead. The fission reaction generates heat, and this heat is transferred, sometimes indirectly, to the water that produces the steam. Consequently, it can be said that the fission reaction in a nuclear plant serves the same purpose – the generation of heat – as the burning of a fossil fuel in a conventional plant. The fission process requires a particular kind of a high atomic number element, such as uranium or plutonium, as a basic material.

For example, naturally-occurring uranium is a mixture of three isotopes, atomic forms that are chemically alike but vary in mass. An atom of one of these isotopes, uranium-235 (^{235}U), can readily undergo fission when a free neutron (an energetic subatomic particle) strikes its heavy central nucleus. The nucleus breaks into two pieces that fly apart at high speed; in addition, two or three new neutrons are released. Thus:



The kinetic energy of the fission fragments is converted to heat when they collide with surrounding atoms, and the released neutrons cause a chain reaction by initiating new fissions in other atoms of uranium.

Sustaining the chain reaction is important because more than 30 billion fissions must occur in one second to release each watt of energy. If the chain reaction is to be useful, the fissions must occur at a desired rate, and the heat that is generated by the process must be removed. Thus, the nuclear reactor provides an environment in which fission reactions can be initiated, sustained, and controlled, and to make possible recovery of the resultant heat.

The essential components of a reactor are: (i) the fuel, which fissions to produce neutrons and to release energy, (ii) the control elements, which are used to set the energy release rate, and (iii) the cooling fluid, which removes the heat generated in the reactor.

See also: Nuclear Reactor, Radioactivity, Steam Turbine.

Nuclear Reactor

A nuclear reactor is a reactor design for nuclear reactions in order to achieve a self-sustained chain reaction with a combination of fissile, fertile, and other materials. Common characteristics useful for classification purposes are (i) the coolant, which is the principle heat removal medium, (ii) the *steam cycle*, which is the number of separate coolant loops, (iii) the *moderator*, which is the material (if any) used to decrease the speed of neutrons produced by fission, (iv) the neutron energy, which is the general energy range for the neutrons that cause most of the fission reactions, and (v) the *fuel production system*, which is referred to as a breeder if the system produces more fuel than it consumes (i.e., the reactor changes from fissile to fertile) and, in such a case, the reactor is said to be a *converter*.

The first two features relate to the current practice of converting fission energy, first to heat and then to electrical energy by employing a steam cycle. Coolants include water, heavy water, gases, and liquid metals. The steam cycles may employ from one to three separate loops, including one for primary coolant circulation and one (not necessarily separate) for steam generation.

Since neutrons are emitted from fission at high energy and the very-low-energy neutrons have a higher likelihood of causing additional fission reactions. Thus, many systems employ a moderator to slow down these neutrons. The best moderators are of low mass, allowing maximum energy transfer through neutron collisions. Typical materials used for this purpose are hydrogen, deuterium (heavy hydrogen, hydrogen-2, ^2H), and carbon. The moderator and coolant may be the same (e.g., water) or may be separate materials (e.g., gaseous coolant and solid graphite moderator). Neutrons with low enough energies to be roughly in thermal equilibrium with the surrounding materials are said to be thermal neutrons, while neutrons at or near fission energies are termed fast neutrons. Fast reactors avoid the use of moderators, such as with a metal coolant like sodium, instead of one of the moderating materials identified above.

Any reactor that contains fertile species such as thorium-232 (^{232}Th), uranium-238 (^{238}U), or plutonium-242 (^{242}Pu) produces some amount of new fissile fuel. Breeder reactors actually produce more fuel than they consume, while converter reactors produce lesser amounts of new fuel.

The various types of nuclear reactor technologies (Table N-4) which all have several components in common such as the fuel, control rods, moderator, and coolant.

Table N-4 Types of nuclear reactors.

Type	Fuel	Moderator	Coolant
CANDU	Uranium	Heavy water*	Heavy water* under pressure
RBMK	Enriched uranium	Carbon (graphite)	Boiling water
BWR	Enriched uranium	Boiling water	Boiling water
PWR	Enriched uranium	Pressurized water**	Pressurized water
Fast reactor	Enriched uranium	None***	Liquid sodium****
Key: CANDU: Nuclear technology developed in Canada. RBMK: Bolchoe molchnastie kipiachie reactor – high-power boiling water reactor. BWR: Boiling water reactor. PWR: Pressurized water reactor.			

*Heavy water – deuterium oxide (D_2O) - water in which the hydrogen atoms of the water molecule (H_2O) have been replaced by deuterium, a heavy isotope of hydrogen.

**In liquid form.

***Neutrons remain fast.

****Does not slow down the neutrons.

Thus, a nuclear reactor is simply a device for starting and controlling a self-sustaining fission chain reaction from which energy for commercial and domestic activities can be produced:

Nuclear reactor	Heat	Electricity
		Hot water
		Hydrogen
		Steam

Nuclear reactors are used in several ways: (i) to supply intense fields or beams of neutrons for scientific experiments, (ii) to produce new elements or materials by neutron irradiation, and (iii) to furnish heat for electric power generation, propulsion, industrial processes, or other applications. There are various types of reactor technologies. Nonetheless, these nuclear reactors all have several components in common such as the fuel, control rods, moderator, and coolant.

The basic parts of a nuclear reactor are (i) the core of fuel, (ii) a neutron moderator which is a material that aids the fission process by slowing down the neutrons so they can collide with the atoms and provoke fission reactions, (iii) a means of regulating the number of free neutrons and thereby controlling the rate of fission, (iv) a means of removing the heat generated in the core, which is typically the purpose of the coolant water, and (v) radiation shielding.

Typically, the reactor containment is made of steel and/or reinforced concrete. It contains the reactor vessel, the primary system, the steam generators, and the main components important to reactor safety. It is leak-tight and designed to prevent leaks from radioactive fuel elements into the environment, particularly in the case of a severe accident like a core meltdown (strong rise in the temperature causing the fuel to melt).

The energy released as heat during the fission of uranium-235 nuclei must be transferred from the reactor core to the systems designed to transform heat into electricity, i.e., the turbine and alternator. This role is guaranteed by the coolant, the fluid used to remove the heat generated by the nuclear fuel. The coolant can be water, a liquid metal (sodium or lead), or a gas (carbon dioxide or helium). The coolant is also used to maintain the fuel temperature at its nominal temperature that is compatible with the resistance of the materials.

A heat exchanger is designed to transfer thermal power from one system to another. In the case of pressurized water reactors (PWRs), for instance, the primary coolant is water which exits the reactor core at a temperature on the order of 330°C (525°F) and is kept at a high pressure on the order of approximately 2,200 psi bar to prevent it from transforming into steam. This water then flows through a steam generator that is used to transfer the thermal power between the primary and secondary systems. They are designed so that the water in the secondary system boils and generates steam. When the steam expands, it drives a turbine that is coupled to an alternator which produces electricity. This system is also known as a power conversion system; thermal energy is converted into mechanical and then electrical energy. A third system is designed to cool and then condense steam.

Evolving from conventional water-cooled reactors, supercritical water-cooled reactor operates at high pressures, above the critical point, to allow for high coolant exit temperatures (up to 625°C, 1,155°F) and high thermal efficiencies. Such a temperature level is suitable for medium temperature process heat applications. Since water systems operate at elevated pressures, intermediate systems will be needed to convert thermal energy to lower pressure fluids used in industrial applications. All of the water-cooled concepts can be used for bottoming cycles that include district heating and desalination.

Gas-cooled reactor concepts include the pebble bed reactor and the prismatic modular reactor. Helium pressures enhance the coolant capacity to transmit heat. The coated particle fuel used in the thermal spectrum concepts is capable of high burnups, and they are easily adjustable to a wide range of fuel cycles. In terms of liquid metal-cooled reactor concepts. Closed fuel cycles are employed for the purpose of maximizing the uranium resource utilization and minimizing the amount of high-level radioactive waste.

In the case of sodium-cooled fast reactors (SFRs), the primary coolant is sodium, which is a liquid metal that exits the core at approximately 550°C (1,020°F) and at low pressure (typically, <100 psi). The power conversion system is based on the same principle as that of a pressurized water reactors insofar as a steam generator produces steam which expands in a turbine coupled to an alternator. The key difference is an additional system interposed between the primary system containing low-pressure sodium and the water-to-steam power conversion system at high pressure. The objective of this intermediary system is to take into account the risk of interaction between sodium and

water by dissociating the radiological risk in the primary system from other risks. Two heat exchangers are therefore required between the primary system and the power conversion system. The fast reactors have the advantage of saving on uranium resources and recycling recoverable materials, plutonium in particular.

Finally, as an additional note as an explanation of the nomenclature currently in use, considering the operating lifetimes of such facilities, reactors belonging to different generations can be defined.

The first generation includes the prototypes and the first industrial-scale reactors used for commercial purposes that were developed in the 1950s and 1960s before being commissioned in the 1970s. During this period, France developed a reactor technology using natural uranium for the fuel since it did not have access to uranium enrichment technologies.

The second generation of nuclear reactors was commissioned from early 1970 onwards. This generation was designed with objectives of improved competitiveness and energy independence at a time when tensions were running high due to the price of fossil fuels (oil crisis). Most of the reactors in current service are second generation.

The third generation focuses on safety and security requirements: consolidated resistance to external hazards such as plane crashes. These reactors have incorporated operating experience from second-generation reactors, from the Three Mile Island and Chernobyl accidents.

The fourth generation refers to reactors currently in design phase which could be deployed on an industrial scale by around 2050. The design incorporates a number of technological breakthroughs with respect to what has been built, and the criteria to be met (in addition to economic considerations) are: (i) sustainability, (ii) nuclear safety, and (iii) resistance to nuclear proliferation.

Nuclear Reactor – Boiling Water Reactor

In the boiling water reactor, water enters the reactor and is heated as it passes up between the elements of nuclear fuel. Soon, steam collects in the upper portion of the reactor and leaves through an outlet pipe. The pipes identified as steam pipes, and water pipes would be connected to those similarly to form a complete power plant.

The water and steam in a typical boiling-water reactor are kept at a pressure of 1,000 pounds per square inch (psi); this is equivalent to the pressure at a depth of approximately one-half mile beneath the surface of the sea. The pressure raises the boiling point of the reactor water to a high value, so that when steam is produced, its temperature and pressure are great enough for efficient use in the turbine.

Steam at the boiling temperature (100°C, 212°F) has too low an energy value for use in a turbine, and in order to increase the energy, the steam temperature must be raised. In a reactor, this is done by operating it at high pressure. At the typical boiling-water reactor pressure of 1,000 psi, the temperature of the steam is on the order of approximately 285°C (545°F). A nuclear steam-supply system based on a boiling-water reactor may appear relatively simple compared with some of the other systems. While the boiling-water system has only a few principal components, these are much larger than those in a pressurized-water system, for example. A central station nuclear power plant with an electrical output of around 800,000 kilowatts requires a boiling-water reactor vessel (the container that holds the nuclear fuel) approximately 70 feet high by 20 feet in diameter. A pressurized-water reactor vessel for a plant of the same capacity is only approximately 40 feet high by 16 feet in diameter. However, there are some additional large components in the pressurized-water system.

Nuclear Reactor – Breeder Reactor

A breeder reactor is a nuclear reactor that has the potential for breeding (i.e., producing more nuclear fuel than the reactor consumes) because of the materials, or combinations of materials, that are used to build the reactor.

For example, a uranium-235 atom can fission when its nucleus absorbs a neutron. The fission reaction releases free neutrons that may, in turn, initiate other fissions. All the neutrons released, however, are not absorbed by fissionable material; some are absorbed in the structural material of the reactor, the control elements, or the coolant; some escape from the reactor and are absorbed by shielding; and some are absorbed by fertile material. When the nucleus of an atom of fertile material absorbs a neutron, the fertile atom can be transformed into an atom of a fissionable

material – the substance that forms the basis for the nuclear chain reaction. By careful selection and arrangement of materials in the reactor—including, of course, fissionable and fertile isotopes – the neutrons not needed to sustain the fission chain reaction can fairly effectively convert fertile material into fissionable material.

The breeder reactor improves the efficiency of the neutron process both by increasing the number of free neutrons released in fission and by decreasing the number of neutrons wasted, thereby making a larger number available for absorption in fertile material. If, for each atom of fissionable material that is consumed, more than one atom of fertile material becomes fissionable material, the reactor is said to be breeding. One fertile material is uranium-238, which is always found in nature with fissionable uranium-235. When uranium-238 absorbs neutrons, it is converted to fissionable plutonium-239. Another fertile material is thorium-232, which can be converted to fissionable uranium-233.

Some of the reactors that are *possible* breeders may not prove capable of breeding in actual practice, but one type has already operated successfully in several plants. This is the liquid-metal-cooled breeder reactor.

Systems and components for the breeder reactor differ from those for other types of reactors. Both the primary reactor coolant system and the intermediate loop use liquid metal because it has excellent heat-transfer and nuclear characteristics; the metal is usually sodium. The liquid metal in the reactor is heated to approximately 535°C (1,000°F), and then goes to the heat exchanger, where it transfers its heat to the liquid metal of the intermediate loop. The metal in the intermediate loop moves to the steam generator, where it heats water to produce steam at a temperature on the order of 480°C (900°F).

Like other coolants, liquid metal has some desirable and some undesirable features. It is good because it does an excellent job of neutron conservation and of removing heat and does not have to be used at high pressure to attain high temperatures. The fuel in a liquid-metal-cooled breeder reactor can be operated at very high-power densities because the heat can be removed readily.

Nuclear Reactor - Decommissioning

Like other types of power plants, nuclear power plants have a lifespan after which they must be retired because the cost of running them becomes too high. The generation of nuclear power plants currently operating was designed to last approximately thirty years. Some plants showed serious levels of deterioration after as few as fifteen years. However, some have lasted well beyond thirty-year expectations. Whenever a power plant—whether coal, natural gas, or nuclear—is retired, it must be demolished and cleaned up so that the site can be used again.

Thus, at some point, the nuclear plants now operating worldwide may need to be retired. Most of them were designed to last approximately thirty years. Some plants showed serious levels of deterioration after as few as fifteen years; some have lasted well beyond their thirty-year expectations. There are three methods of retiring, or decommissioning, a reactor: (i) safe enclosure, (ii) entombment, and (iii) immediate dismantling.

Safe enclosure, or mothballing, involves removing the fuel from the plant, monitoring any radioactive contamination (which is low or nonexistent), and guarding the structure to prevent anyone from entering until eventual dismantling and decontamination activities occur. Entombment, which was used at Chernobyl, involves permanently encasing the structure in a long-lived material such as concrete. This procedure allows the radioactive material to remain safely on-site. Immediate dismantling involves decontaminating and tearing down the facility within a few months or years. This method is initially more expensive than the other options but removes the long-term costs of monitoring both the structure and the radiation levels. It also frees the site for other uses, including the construction of another nuclear power plant. Nuclear power companies are also seeking alternative uses for nuclear shells, including the conversion of old nuclear plants to gas-fired plants.

Nuclear Reactor – Fast Neutron Reactor

A fast-neutron reactor (FNR) or simply a fast reactor is a category of nuclear reactor in which the fission chain reaction is sustained by fast neutrons (carrying energies above 0.5 MeV or greater), as opposed to thermal neutrons

used in a thermal neutron reactor. This type of reactor does not need a neutron moderator but requires a fuel that is relatively rich in fissile material when compared to that required for a thermal neutron reactor.

A fast-neutron reactor can reduce the total radiotoxicity of nuclear waste by using all or almost all of the waste as fuel. With fast neutrons, the ratio between splitting and the capture of neutrons by plutonium and the minor actinide elements is often larger than when the neutrons are slower, at thermal or near-thermal epithermal speeds.

The transmuted even-numbered actinide elements (such as ^{240}Pu , ^{242}Pu) split nearly as easily as odd-numbered actinides in fast reactors. After they split, the actinides become a pair of fission products which have a reduced total radiotoxicity. Since disposal of the fission products is dominated by the most radiotoxic fission products strontium-90 (^{90}Sr), which has a half-life of 28.8 years, and caesium-137 (^{137}Cs) which has a half-life of 30.1 years, the result is to reduce nuclear waste lifetimes from tens of millennia (from transuranic isotopes) to a few centuries. The processes are not perfect, but the remaining transuranic elements are reduced from a significant problem to a tiny percentage of the total waste, because most of the transuranic elements can be used as fuel.

A fast reactor technically solves the fuel shortage without assuming undiscovered reserves, or extraction from dilute sources such as granite or seawater. They permit nuclear fuels to be bred from almost all the actinides, including known, abundant sources of depleted uranium and thorium, and light-water reactor wastes. On average, more neutrons per fission are produced by fast neutrons than from thermal neutrons. This results in a larger surplus of neutrons beyond those required to sustain the chain reaction. These neutrons can be used to produce extra fuel, or to transmute long half-life waste to less troublesome isotopes, or some can be used for each purpose. Though conventional thermal reactors also produce excess neutrons, fast reactors can produce enough of them to breed more fuel than they consume.

Nuclear Reactor – Gas-Cooled Reactor

The flow scheme for a gas-cooled reactor in bears a strong resemblance to the diagram for a pressurized-water reactor. The principle of operation is the same for both types of reactor insofar as a working fluid transports heat from the reactor to the steam generator, where the heat makes steam for the turbine.

In a gas-cooled reactor, the working fluid is a gas, usually helium or carbon dioxide at a pressure of a several hundred psi, is circulated through the reactor, the piping, and the steam generator by a blower (fan). The energy required to drive the blowers (there would be several) for the reactor of an 800,000-kilowatt power plant would operate 400,000 20-inch window fans. Also, there is a moderator which is a substance put in a reactor to slow the neutrons and increase the effectiveness in causing fissions. In water-cooled reactors, it is not necessary to add solid moderator components, because the cooling water serves this purpose. Gas is not a good moderator; however, in gas-cooled reactors, a special material, usually graphite, is built in. Graphite is a natural choice because it can withstand the high temperatures that exist in gas-cooled reactors (in some, the gas is heated to approximately 760°C ($1,400^{\circ}\text{F}$)). The high operating temperatures are put to good use. Steam as hot as approximately 535°C ($1,000^{\circ}\text{F}$) is produced; at this temperature and at the high pressure that goes with it, the steam can drive a turbine.

In addition to the high-temperature performance, a gas-cooled reactor has the desirable characteristic of low net fuel consumption; very advanced models, in fact, may be able to produce more fuel than they consume.

Nuclear Reactor – Heavy Water Reactor

Heavy water (D_2O) is usually used in tube-type reactors, in which the nuclear fuel is positioned inside process tubes that penetrate a tank. The tank contains the heavy water, which surrounds the fuel-containing tubes and acts as a moderator, much as graphite does in gas-cooled reactors. The fuel is in a form that does not occupy all the space in the process tubes, so there is room for a cooling fluid to flow along the fuel elements and remove the heat that is generated.

Any of several cooling fluids – organic compounds, gas, water, or heavy water – can be used in heavy-water reactors, since the heavy-water moderator is separated from the cooling fluid by the walls of the process tubes.

Temperatures in heavy-water reactors depend upon the kind of cooling fluid used, among other things, but steam hotter than 370°C (700°F) can be produced.

In terms of nuclear fuel utilization, the heavy-water reactor is an interim type: Its net fuel consumption is quite low, and it can operate on natural uranium, which makes it attractive to use in some countries.

Nuclear Reactor – Pressurized Water Reactor

A pressurized-water reactor operates at conditions under which the water passing through the reactor does *not* boil. Pressure in the reactor and the piping loop connected to it is on the order of 2,250 psi, or more than twice the pressure in a boiling-water reactor. This high pressure permits the water to be heated to 315°C (600°F) without boiling. The heated water goes to a steam generator that, as the name implies, makes the steam that drives the turbine.

In the steam generator, the hot reactor water passes through tubes that are surrounded by water from the turbine portion of the plant; this water is at a pressure well below that of the reactor water system. The tubes containing hot reactor water heat the surrounding water and make steam, which goes to the turbine at a temperature on the order of 260°C (500°F). The reactor water leaving the steam generator has been cooled by giving up some of this heat, so it is pumped through the reactor to be heated again and start another cycle.

A nuclear steam supply that uses a pressurized-water reactor consists of two separate water systems that meet in the steam generator. The water in one system does not mix with that in the other, but heat is transferred from the reactor system to the steam system.

Nuclear Safety

One of the issues that raise public concern related to anything connected with the term nuclear energy (or energy from nuclear sources) is the concern that a nuclear reactor might get out of control and melt down.

Unlike a fission power plant, which contains a large quantity of uranium or plutonium fuel, enough to keep it going for many years, a fusion power plant contains only a small amount of deuterium fuel (^2H or D_2) and tritium fuel (H^3 or T_3). Typically, there is approximately 1 gram of fuel which is sufficient to maintain the reaction for only a several few seconds, and if fuel is not continually replaced, the fusion reaction ceases.

A second consideration is the radioactive waste. A fission reactor produces two types of radioactive waste. The most difficult to process and store are the waste products that result from the fission fuel cycle – these are intensely radioactive substances that need to be separated from the unused fuel and then stored safely for tens of thousands of years. The fusion fuel cycle produces none of these radioactive waste products – the waste product is helium gas, which is not toxic or radioactive. The tritium fuel itself is radioactive, but it decays relatively quickly (the half-life is 12.3 years). Moreover, all of the tritium fuel that is produced will be recycled quickly and burned in the power plant.

An important safety feature is that there need be no shipments of radioactive fuels into or out of the fusion plant. The raw materials necessary for the fusion fuel, lithium and water, are completely nonradioactive. There is enough lithium to last for at least tens of thousands of years and enough deuterium in the oceans to be truly inexhaustible. Moreover, these raw materials are widely distributed, making it impossible for anyone in the country to corner the market. More advanced types of fusion may be developed in the long term to burn only deuterium.

The second source of waste from a nuclear power plant is the structure of the reactor – this is made radioactive by the neutrons emitted during the nuclear reactions. Fusion and fission are broadly similar in this respect, and some components of the structure of a fusion power plant will become intensely radioactive. Components that have to be removed for repair or replacement will have to be handled using remote robots and stored inside massive concrete shields. However, the lifetime of these structural wastes is much shorter than that of fission fuel waste products. At the end of its working life, a fusion power plant will have to be shielded before it can be demolished.

Nuclear Waste Management

The single most troubling issue for the nuclear power industry is waste management. Nuclear wastes can be classified into two general categories, low-level wastes and high-level wastes. The former consist of materials that release a relatively modest level of radiation and/or that will soon decay to a level where they no longer present a threat to humans and the environment. Storing these materials in underground or underwater reservoirs for a few years or in some other system is usually a satisfactory way of handling these materials.

High-level wastes are a different matter. After a period of time, the fuel rods in a reactor are no longer able to sustain a chain reaction and must be removed. These rods are still highly radioactive, however, and present a serious threat to human life and the environment that can be expected to last for tens of thousands of years. These rods and any materials derived from them (as, for example, during chemical dismantling of the rods to extract their plutonium for the production of nuclear weapons or for use as a nuclear fuel), are considered high-level wastes.

Occidental Flash Pyrolysis Process

The Occidental Flash Pyrolysis process (originally called the Garrett process) was designed to pyrolyze coal particles at a temperature not in excess of 760°C (1,400°F) in an entrained system to produce a liquid product, char, and gas.

The process utilizes the concept of short residence time of the feed coal, thereby increasing the throughput of coal per unit of cross-sectional area with the subsequent higher production of liquid products. Milled and screened coal is transported to the reactor by hot nitrogen where recycled hot char heats the coal rapidly to 510 to 730°C (950 to 1,350°F). A portion of the char product is cooled (as product), but the remainder is heated in a partial oxidation (burning) process to raise its temperature to 650 to 925°C (1,200 to 1,700°F) for recycle to the reactor. Cyclones remove fine char particles from the pyrolysis overhead prior to quenching in the collector system. This system consists of two tar recovery stages and a vacuum flash unit. In the first recovery stage, the pyrolysis vapor is condensed by quenching at approximately 99°C (ca. 210°F) to remove the majority of the heavier constituents; cooling to approximately 25°C (80°F) in the second stage causes water and low-boiling oils to condense. The vacuum flash unit is employed to separate the higher boiling constituents into fractions of varying volatility.

The process can accept a diversity of organic feedstocks to produce as its liquid products and offers potential for use with various biomass feedstocks. The char and **pyrolysis** gas produced as by-products are burned on-site for **process** heat.

See also: Liquefaction.

Ocean Currents

Currents exist at all depths in the ocean; in some regions, two or more currents flow in different directions at different depths. Although the current system is complex, ocean currents are driven by two forces: the Sun and the rotation of the Earth.

The Sun affects the ocean in two ways. First, the Sun heats the atmosphere, creating winds and moving the sea surface through friction which tends to drag the water surface along as the wind blows over it. Although the wind strongly affects the surface layer, its influence does not extend much below approximately 325 feet in depth. Second, the Sun alters the density of the ocean surface water directly by changing its temperature and/or the salinity. If water is cooled or becomes saltier through evaporation, it becomes denser. This can result in the water column becoming unstable, setting up density-dependent currents, also known as the thermohaline circulation.

The rotation of the Earth also affects the currents through the Coriolis force which causes water to move to the right in the Northern Hemisphere and to the left in the Southern Hemisphere. It exists because moving ocean water is affected by friction with the Earth only at the seafloor, and because the eastward linear velocity of the Earth decreases from a maximum at the equator to zero at the poles (the rotational velocity, however, does not change). A parcel of water at the equator is moving at the same speed as the Earth. If it starts to move north, with no friction, it is then going faster than the Earth beneath it. To conserve momentum (the product of mass and velocity), it consequently moves more to the east as it gets farther from the equator. The Coriolis force therefore increases away from the equator.

Patterns of Surface Currents

The movement of sea water between layers of varying temperature and density. Ocean circulation is produced by convection, with warm currents traveling away from the Equator, cooler water moving from the poles. In the Southern Hemisphere, the oceanic currents move in an anti-clockwise system, whereas in the Northern, the system is clockwise, an effect caused by the rotation of the Earth.

The general pattern of surface currents shows a series of quasi-circular gyres (circular or spiral motions or forms), or large eddies, in each ocean basin. The gyres tend to be biased toward the western side of the basin, where strong, narrow

flows are found in the Gulf Stream current, the Kuroshio current, the Agulhas current, the Brazilian current, and East Australian current, which flow at speeds up to 6 miles per hour. Current speeds away from the western boundaries of the gyres are generally much lower, and currents on the eastern boundaries of ocean basins are much wider.

The gyres rotate clockwise in the Northern Hemisphere and counterclockwise in the Southern Hemisphere because of the Coriolis force; in this, they follow the prevailing wind patterns. The gyres in both ocean and atmosphere help to transport heat away from the equator toward the poles (the Gulf Stream keeps northern Europe considerably warmer than its latitude suggests). This northward flow of warm water in the North Atlantic and a similar flow (the Kuroshio) in the North Pacific are partly balanced by southward flow in the East Greenland and Labrador Currents and in the Oyashio, respectively, while additional southward flow occurs at greater depths. The surface equatorward flow along the eastern edges of the gyres is also considerably cooler than the poleward flow found on the western boundaries. This results from wind-driven upwelling; the equatorward wind stress caused by the trade winds push water away from the coast and cooler subsurface water upwells to replace it.

Gyral motion is also absent near the equator. Equatorial currents are also driven by the wind, in particular by the trade winds – from the northeast in the Northern Hemisphere and from the southeast in the Southern Hemisphere. However, the Coriolis force here is zero, even though it becomes significant within one degree of latitude north or south. The boundary between the two sets of trade winds is usually slightly north of the equator. The trade winds set up two westward-flowing currents north and south of the equator (the North and South Equatorial Currents), but because the southeast trades blow across the equator, this causes a divergence (upwelling) along the equator itself because of the change in direction of the action of the Coriolis force.

Between the two trade-wind belts is a region of generally light winds, known as the Doldrums. This allows water, which would otherwise pile up against the western boundary of the ocean in the Equatorial currents, to flow back eastwards in the surface Equatorial Countercurrent. There is also an eastward-flowing equatorial undercurrent, which forms a jet within the thermocline, driven by the horizontal pressure gradient. This system of eastward-flowing and westward-flowing currents is found in the upper 650 feet in all three oceans, although their distribution may change seasonally.

Deep Currents

Currents in the deep ocean exist because of changes in the density of sea water occurring at the surface. These density changes give rise to specific water masses, which have well-defined temperature and salinity characteristics, and which can be traced for long distances in the ocean.

When sea water freezes, much of the salt that it contains is frozen out, so that a layer of cold brine forms at the ocean surface. Being denser than the water below it, the brine sinks, entraining water as it does so, until it reaches a level where it has the same density as the surrounding sea water. This process takes place in several regions of the world's oceans, the most important being in the Greenland, Norwegian, and Labrador Seas in the Northern Hemisphere, and close to the Antarctic continent in the Weddell and Ross Seas in the south.

Role of Water Masses

All these water masses help to transfer oxygen from the atmosphere into the deep ocean. The sinking water is very cold and contains high concentrations of dissolved oxygen acquired at the surface, because cold water can hold more oxygen than warm water. During their flow, they mix with “older” water that has been away from the surface for a longer time, thus ensuring that the bottom waters of the ocean are supplied with oxygen. Additional oxygen is supplied in the southern hemisphere by Antarctic Intermediate Water, formed in a band near 50° S to 55° S latitude. In this region, water does not freeze in winter, but it does cool forming a low salinity layer that sinks to approximately 1,000 meters (0.6 mile) depth and moves north in all three oceans.

Ocean Energy

The ocean can produce two types of energy: (i) thermal energy from the heat of the Sun and (ii) mechanical energy from the tides and waves. The heat of the Sun warms the surface water a lot more than the deep ocean water, and this temperature difference creates thermal energy.

There are three types of electricity conversion systems: (i) the closed-cycle system, (ii) the open-cycle system, and (iii) the hybrid system. Closed-cycle systems use the ocean's warm surface water to vaporize a working fluid, which has a low-boiling point, such as ammonia. The vapor expands and turns a turbine which then activates a generator to produce electricity. Open-cycle systems actually boil the seawater by operating at low pressures which produces steam that passes through a turbine/generator. A hybrid system combines both closed-cycle and open-cycle systems.

Ocean mechanical energy is different from ocean thermal energy. Even though the sun affects all ocean activity, tides are driven primarily by the gravitational pull of the moon, and waves are driven primarily by the winds. As a result, tides and waves are intermittent sources of energy, while ocean thermal energy is fairly constant. Also, unlike thermal energy, the electricity conversion of both tidal and wave energy usually involves mechanical devices.

The three most developed technologies derive (i) energy from tides, (ii) energy from waves, and (iii) ocean thermal energy conversion (OTEC) and are described below.

Tidal Energy

Tidal power is not a new concept, and has been used since the eleventh century to turn water wheels. Presently, power is generated from tides in a manner similar to hydroelectric power plants. In the process of deriving energy from tides, a dam (sometimes referred to as a barrage) is built across an estuary with gates, and turbines installed at regular intervals along the barrage are opened when there is significant difference in water elevation on either side of the barrage. Water flows through the turbines, and electricity is produced. This method can be used for water flowing both into and out of the estuary.

Although tidal power generation can offer some advantages, including reducing greenhouse gas emissions by not using fossil fuels, there are some significant environmental disadvantages. The construction of a tidal dam in an estuary will change the tidal level in the basin. This change will have a marked effect on the turbidity (cloudiness) of the water and sedimentation within the basin, which in turn affects navigation and recreation. An altered tidal level will also have an effect on the local marine food chain. However, because very few tidal barrages have been built, little is understood about the full impact of tidal power systems on the local environment, and it is evident that its effects greatly depend on the local geography and marine ecosystem.

Wave Energy

Wave energy generation devices fall into two general classifications: fixed and floating. Fixed generating devices, which are mounted either to the seabed or shore, have some significant advantages over floating systems, particularly in the area of maintenance. However, the number of suitable sites available for fixed devices is limited.

The oscillating water column, a fixed device built on shore, generates electricity in a two-step process. As a wave enters and leaves the column, the water in the column rises and falls, which in turn forces air back and forth through a turbine at the top of the column. This is a simple device, but it is difficult to build and anchor so that it is able to withstand the roughest sea conditions and yet generate a reasonable amount of power from small waves.

Another fixed device, the tapered channel system (TAPCHAN), consists of a tapered channel that feeds into a reservoir constructed on a cliff. The narrowing of the channel causes the waves to increase their amplitude (wave height) as they move toward the cliff face. The waves eventually break over the walls of the channel and into a reservoir, which is positioned several meters above mean sea level. The stored water in the reservoir is then fed through a turbine and generates electricity in the manner of an hydroelectric dam.

Floating-wave energy devices generate electricity through the harmonic motion of the floating part of the device, and are extremely efficient. In these systems, electricity is generated through the rise and fall of the waves.

There are three types of ocean thermal energy conversion processes: closed-cycle, open-cycle, and hybrid-cycle. In the closed-cycle system, heat transferred from the warm surface sea water causes a "working fluid" (such as ammonia, which boils at a temperature of approximately 25°C (77°F), at atmospheric pressure) to turn to vapor. The expanding vapor drives a turbine attached to a generator that produces electricity. The working fluid passes through a condenser and turns back into a liquid that is then recycled through the system.

Ocean Thermal Energy Conversion

The open-cycle ocean thermal energy conversion (OTEC) process uses the warm surface water itself as the working fluid. The water vaporizes in a near vacuum at surface water temperatures. The expanding water vapor drives

a turbine attached to a generator and produces electricity. The water vapor, which has lost its salt and is almost pure fresh water, is condensed back into a liquid by exposure to cold temperatures from deep-ocean water. If the condenser keeps the vapor from direct contact with sea water, the condensed water can be used for drinking water, irrigation, or aquaculture. A direct contact condenser produces more electricity, but the vapor is mixed with cold sea water and the discharge water is salty and is returned to the ocean. The process is repeated with a continuous supply of warm surface sea water. Hybrid systems use parts of both open-cycle and closed-cycle systems to optimize the production of electricity and fresh water.

See also: Geothermal Energy, Hydroelectric Power, Tidal Energy, Wave Energy.

Octane Number

The gasoline performance and hence quality of an automobile gasoline is determined by its resistance to knock, for example, *detonation* or *ping* during service. The antiknock quality of the fuel limits the power and economy that an engine using that fuel can produce: the higher the antiknock quality of the fuel, the more the power, and efficiency of the engine.

In the early days of automobile engine development, there was a demand for more powerful engines and knocking was not a problem. This demand for more powerful engines was met at first by adding more and larger pistons to the engines; some were even built with 16 cylinders. However, the practical limit to the size to which an engine could be built meant that other avenues to increased power had to be explored. The obvious method of getting more power from an engine of given size was to increase its compression ratio (a measure of the extent to which the gasoline-air mixture is compressed in the cylinder of an engine). The more the mixture is compressed before ignition, the more power the engine can deliver, but the increased performance was accompanied by an increased tendency for detonation or *knocking*. Eventually, the cause of engine knock was traced to the gasoline. Since some gasolines seemed to cause more knock than another, and since there was no suitable testing procedure, it was difficult to determine the relative antiknock characteristics of gasoline. It appeared, however, that cracked gasoline caused less knock than straight-run gasoline and, hence, the use of cracked gasoline as a fuel increased.

In 1922, tetraethyl lead was discovered to be an excellent antiknock material when added in small quantities to gasoline, and gasoline containing tetraethyllead became widely available. However, the problem of how to increase the antiknock characteristics of cracked gasoline became acute in the 1930s. One feature of the problem concerned the need to measure the antiknock characteristics of gasoline accurately. This was solved in 1933 by the general use of a single-cylinder test engine, which allowed comparisons of the anti-knock characteristics of gasoline to be made in terms of octane numbers. The octane numbers formed a scale ranging from 0 to 100: the higher the number, the greater the antiknock characteristics. In 1939, a second and less severe test procedure using the same test engine was developed, and results obtained by this test were also expressed in octane numbers.

Octane numbers are obtained by the two test procedures, those obtained by the first method are called *motor octane numbers* (indicative of high-speed performance) (ASTM D2700 and ASTM D2723). Those obtained by the second method are called *research octane numbers* (indicative of normal road performance) (ASTM D2699 and ASTM D2722). Octane numbers quoted are usually, unless stated otherwise, research octane numbers.

In the test methods used to determine the antiknock properties of gasoline, comparisons are made with blends of two pure hydrocarbon derivatives, *n*-heptane and *iso*-octane (2,2,4-trimethylpentane). *Iso*-octane has an octane number of 100 and is high in its resistance to knocking; *n*-heptane is quite low (with an octane number of 0) in its resistance to knocking.

The anti-knock characteristics of an additive are typically evidenced by an increase in the motor and research octane numbers of the base fuel when the additive is admixed therewith. The motor (MON) and research (RON) octane numbers of fuel compositions are typically measured by ASTM D 2700 and ASTM D 2699, respectively. While motor and research octane numbers are themselves good indicators of the anti-knock characteristics of an additive, another measure of the anti-knock characteristics of an additive is the average of the two numbers $(RON + MON)/2$. This average provides a fairly good approximation of the octane number required by engines under typical driving conditions, in that MON is a more severe test, with higher compression and temperature, than RON. Furthermore, this average is the typical rating used for commercial fuel products.

Extensive studies of the octane numbers of individual hydrocarbon derivatives have brought to light some general rules. For example, normal paraffins have the least desirable knocking characteristics, and these become progressively worse as the molecular weight increases. *Iso*-paraffins have higher octane numbers than the corresponding normal isomers, and the octane number increases as the degree of branching of the chain is increased. Olefins have markedly higher octane numbers than the related paraffin derivatives; naphthene derivatives are usually better than the corresponding normal paraffin derivatives but rarely have high octane numbers; aromatic derivatives usually have high octane numbers.

Blends of *n*-heptane and *iso*-octane thus serve as a reference system for gasoline and provide a wide range of quality used as an antiknock scale. The exact blend, which matches identically the antiknock resistance of the fuel under test, is found, and the percentage of *iso*-octane in that blend is termed the *octane number* of the gasoline. For example, gasoline with a knocking ability which matches that of a blend of 90% *iso*-octane and 10% *n*-heptane has an octane number of 90. However, many pure hydrocarbon derivatives and even commercial gasoline have an anti-knock quality above an octane number of 100. In this range, it is common practice to extend the reference values by the use of varying amounts of tetraethyllead in pure *iso*-octane.

With an accurate and reliable means of measuring octane numbers, it was possible to determine the cracking conditions – temperature, cracking time, and pressure – that caused increases in the antiknock characteristics of cracked gasoline. In general, it was found that higher cracking temperatures and lower pressures produced higher octane gasoline, but unfortunately more gas, cracked residua, and coke were formed at the expense of the volume of cracked gasoline.

To produce higher-octane gasoline, cracking coil temperatures were pushed up to 510°C (950°F), and pressures dropped from 1,000 to 350 psi. This was the limit of thermal cracking units, for at temperatures over 510°C (950°F), coke formed so rapidly in the cracking coil that the unit became inoperative after only a short time on-stream. Hence, it was at this stage that the nature of the gasoline-producing process was reexamined, leading to the development of other processes, such as reforming, polymerization, and alkylation for the production of gasoline components having suitably high octane numbers.

It is worthy of note here that the continued decline in crude oil reserves and the issue of environmental protection have emerged as of extreme importance in the search for alternatives to crude oil. In this light, oxygenates, either neat or as additives to fuels, appear to be the principal alternative fuel candidates beyond the crude oil refinery.

Octane Rating

The octane rating of a fuel is the knock resistance (anti-knock rating) compared to a mixture of *iso*-octane (2,2,4-trimethylpentane, an isomer of octane) and *n*-heptane. By definition, *iso*-octane is assigned an octane rating of 100 and heptane is assigned an octane rating of zero. An 87-octane gasoline, for example, possesses the same anti-knock rating of a mixture of 87% (by volume) *iso*-octane and 13% (by volume) *n*-heptane. This does not mean, however, that the gasoline actually contains these hydrocarbon derivatives in these proportions. It simply means that it has the same autoignition resistance as the described mixture.

The octane rating does not relate to the energy content of the fuel nor the speed at which the flame initiated by the spark plug propagates across the cylinder. It is only a measure of the resistance of the fuel to autoignition. It is for this reason that one highly branched form, or isomer, of octane (2,2,4-trimethylpentane) has (by definition) an octane rating of 100, whereas *n*-octane has an octane rating of -10, even though the two fuels have exactly the same chemical formula.

The most common type of octane rating worldwide is the Research Octane Number (RON) which is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of *iso*-octane and *n*-heptane.

The Motor Octane Number (MON) is a better measure of how the fuel behaves when under load. MON testing uses a similar test engine to that used in RON testing, but with a preheated fuel mixture, a higher engine speed, and variable ignition timing to further stress the knock resistance of the fuel. Depending on the composition of the fuel, the MON of a modern gasoline will be approximately 8 to 10 points lower than the RON. Normally, fuel specifications require both a minimum RON and a minimum MON.

The octane ratings of n-heptane and iso-octane are exactly 0 and 100, by definition. For some other hydrocarbon derivatives, the ratings are variable (Table O-1).

Table O-1 Octane ratings of various hydrocarbon derivatives in order of increasing rating.

Hydrocarbon	Octane rating
n-octane	-10
n-heptane	0
2-methyl heptane	23
n-hexane	25
2-methylhexane	44
1-heptene	60
n-pentane	62
1-pentene	84
n-butane	91
cyclohexane	97
iso-octane	100
benzene	101
Methane	107
Ethane	108
Toluene	114
Xylene	117

Using a fuel with a higher octane lets an engine run at a higher compression ratio without having problems with knock. Actual compression in the combustion chamber is determined by the compression ratio as well as the amount of air restriction in the intake manifold (manifold vacuum) as well as the barometric pressure, which is a function of elevation and weather conditions.

Oil-Bearing Plants

Oil-bearing plants are the plants which produce seeds that can be crushed on the farm to produce a range of vegetable oils, and although they are not good enough for human consumption, they can be used to power motors and onsite generators like those used for combined heat and power plants (CHP).

Oils, Fats, and Waxes

Oils, fats, and waxes are common constituents of plants and usually consist of terpene hydrocarbon derivatives and their derivatives or alcohols, acids, and esters.

Oils occur in much greater concentrations in fruits and seeds. The so-called essential oils are usually sweet, or aromatic-smelling organic compounds which may also contain sulfur and nitrogen in addition to the usual carbon

and hydrogen. These oils are often of the terpene class with the general formula $(C_5H_8)_n$, where $n > 1$, or may be compound types similar to camphor or other oxidation products associated with the basic terpene structure.

Alternately, oils found in plants may also be of the fatty acid or glyceride type or may even be esters of the higher monohydric alcohols and fatty acids. The acids most commonly found as glycerides, or esters in plants are:

$C_{15}H_{31}COOH$	Palmitic acid
$C_{17}H_{35}COOH$	Stearic acid
$C_{17}H_{33}COOH$	Oleic acid

In the glycerides, any of the above fatty acids can combine with glycerol to yield a symmetrical glyceride in which the acid radicals are the same:

$CH_2OCOC_{15}H_{31}$	$CH_2OCOC_{17}H_{35}$
$CHOCOC_{15}H_{31}$	$CHOCOC_{17}H_{35}$
$CH_2OCOC_{15}H_{31}$	$CH_2OCOC_{17}H_{35}$
Tripalmitin	Tristearin

Different fatty acids may combine with one molecule of glycerin to produce a mixed glyceride, e.g.,:

$CH_2OCOC_{17}H_{35}$	$CH_2OCOC_{17}H_{35}$
$CHOCOC_{17}H_{35}$	$CHOCOC_{17}H_{35}$
$CH_2OCOC_{15}H_{31}$	$CH_2OCOC_{17}H_{35}$
Palmitodistearin	Oleodistearin

Vegetable oils and fats are usually liquids or semisolids at ambient temperature and may not actually possess a well-defined melting point. There are many other fatty acids (other than palmitic, stearic, and oleic acids) which are found in plant tissue which may have also been incorporated into the coal precursor, thereby complicating the contribution from the fatty acids still further.

A group of chemical compounds which falls under the general classification sterols also occurs in animal and plant oils and in fats. The structure of the sterols is based on the multi-ring perhydrocyclopentaphenanthrene skeleton.

Sterols are crystalline compounds and contain a hydroxyl group (e.g., cholesterol). They occur either in the uncombined form or as esters of the higher fatty acids and can be isolated from the unsaponifiable portion of oils and fats. Sterols (or the related compounds, the steroids) also occur in animal tissue. In these cases, the compound may actually be cholesterol or the hydroxyl group or the alkyl side chain may have been altered to afford a structurally related compound. The majority of the steroid-type material that contributed to the coal substance may not have arisen from animal remains and that the majority of the steroid-type material which eventually became part of the coal substance arose from plant debris.

Waxes often occur naturally as high-molecular-weight alcohols and esters, although free fatty acids may also occur within this group. The constitution of the natural waxes is a contrast to the so-called crude oil wax, which is actually a mixture of straight-chain paraffin hydrocarbon derivatives containing more than seventeen carbon atoms and which are also solid at room temperature but which do not contain any oxygen functional groups.

The structural chemistry of the natural waxes is somewhat less well defined than the structural chemistry of the oils and fats (glycerides). The more common straight-chain materials are defined by their names, e.g., octacosanol, 28-carbon alcohol, but there is still some doubt related to the structures of some of the less conventionally named natural waxes.

Okra

Okra (sometimes written as Okro, *Abelmoschus esculentus*), known in many English-speaking countries as ladies' fingers or ochro, is a flowering plant in the mallow family. Okra is a crop with considerable potential as an oil seed,

but the growth habits of most cultivars currently grown make harvesting for seed impractical. Okra ripens one pod at a time on each stalk over a period of 2 or 3 months. When ripe, the pods of most cultivars dehisce and most of the seeds either fall out or are rain damaged. The data show the potential for oil and oil seed meal production by okra. The yields of combine-harvested okra seed were only approximately 25% as great. Research by nutritionists has shown that okra meal may be useful as a human food source.

Olamine

An olamine is a compound such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) that is widely used in gas processing (Table O-2).

Ethanolamine (2-aminoethanol, monoethanolamine, ETA, or MEA) is an organic chemical compound with the formula $\text{HOCH}_2\text{CH}_2\text{NH}_2$ ($\text{C}_2\text{H}_7\text{NO}$). The molecule is bifunctional containing both a primary amine ($-\text{CH}_2\text{NH}_2$) and a primary alcohol function ($-\text{CH}_2\text{OH}$).

Table O-2 Olamines used for gas processing.

Olamine	Formula	Derived name	Molecular weight	Specific gravity	Melting point, C	Boiling point, C	Flash point, C	Relative capacity %
Ethanolamine	$\text{HOC}_2\text{H}_4\text{NH}_2$	MEA	61.08	1.01	10	170	85	100
Diethanolamine	$(\text{HOC}_2\text{H}_4)_2\text{NH}$	DEA	105.14	1.097	27	217	169	58
Triethanolamine	$(\text{HOC}_2\text{H}_4)_3\text{N}$	TEA	148.19	1.124	18	335, d	185	41
Diglycolamine	$\text{H}(\text{OC}_2\text{H}_4)_2\text{NH}_2$	DGA	105.14	1.057	-11	223	127	58
Diisopropanolamine	$(\text{HOC}_3\text{H}_7)_2\text{NH}$	DIPA	133.19	0.99	42	248	127	46
Methyldiethanolamine	$(\text{HOC}_2\text{H}_4)_2\text{NCH}_3$	MDEA	119.17	1.03	-21	247	127	51

d: with decomposition

Like other amines, monoethanolamine is a weak base and this property makes it favorable for gas scrubbing. Solutions of monoethanolamine (MEA) in water are used as a gas stream scrubbing liquid in amine treating units. For example, aqueous monoethanolamine is used to remove carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from various gas streams. The monoethanolamine ionizes dissolved acidic compounds, making them polar and having an increased solubility. The monoethanolamine scrubbing solutions can be recycled through a regeneration unit. When heated, monoethanolamine (being a rather weak base) will release dissolved carbon dioxide gas or hydrogen sulfide gas, thereby regenerating the monoethanolamine.

See also: Gas Cleaning, Gas Processing, Gas Treating, Olamine Processes.

Olamine Processes

An olamine process is a process that uses an amine derivative (an olamine) to remove acid gas from natural gas streams.

Ethanolamine derivatives became available commercially in the early 1930s; they assumed steadily growing commercial importance as intermediates after 1945, because of the large-scale production of ethylene oxide. Since the mid-1970s, economical production of very pure, colorless ethanolamines has been possible. Ethanolamine derivatives are produced on an industrial scale exclusively by reaction of ethylene oxide and excess ammonia. This reaction takes place slowly, but is accelerated by water. An anhydrous procedure uses a fixed-bed ion-exchange resin catalyst.

Acid gas removal is an important process in various branches of the hydrocarbon processing industry, primarily in natural gas processing and refining. Acid gas removal is also an essential part of other processes, such as coal

gasification where carbon dioxide, hydrogen sulfide, carbonyl sulfide, mercaptan derivatives, and other contaminants need to be removed. Acid gas is defined as gas containing significant amounts of contaminants, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), and other acidic gases. Sour gas is gas contaminated with hydrogen sulfide, and, thus, gas sweetening refers to hydrogen sulfide removal, because it improves the odor of the gas being processed, while the term acid gas removal refers to the removal of both hydrogen sulfide and carbon dioxide. Acid gases need to be removed in order to comply with sales gas quality regulations. One such treatment for acid gas removal involves the use of ethanolamine derivatives, especially triethanolamine (TEA).

The most commonly used technique for gas processing is to first direct the gas flow through a tower containing an amine (olamine) solution. Amines absorb sulfur compounds from natural gas and can be reused repeatedly. After desulfurization, the gas flow is directed to the next section, which contains a series of filter tubes. As the velocity of the stream reduces in the unit, primary separation of remaining contaminants occurs due to gravity. Separation of smaller particles occurs as gas flows through the tubes, where they combine into larger particles which flow to the lower section of the unit. Further, as the gas stream continues through the series of tubes, a centrifugal force is generated which further removes any remaining water and small solid particulate matter.

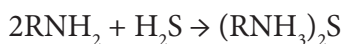
The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems. In many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form.

The general process flow diagram for an amine sweetening plant varies little, regardless of the aqueous amine solution used as the sweetening agent. The sour gas containing hydrogen sulfide and/or carbon dioxide will nearly always enter the plant through an inlet separator (scrubber) to remove any free liquids and/or entrained solids. The sour gas then enters the bottom of the absorber column and flows upward through the absorber in intimate counter-current contact with the aqueous amine solution, where the amine absorbs acid gas constituents from the gas stream. Sweetened gas leaving the top of the absorber passes through an outlet separator and then flows to a dehydration unit (and compression unit, if necessary) before being considered ready for sale.

The primary process for sweetening sour natural gas is quite similar to the processes of glycol dehydration and removal of natural gas liquids by absorption. In this case, however, amine (*olamine*) solutions are used to remove the hydrogen sulfide (the *amine process*). The sour gas is run through a tower, which contains the olamine solution. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. Like the process for the extraction of natural gas liquids and glycol dehydration, the amine solution used can be regenerated for reuse.

Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) are the most widely used *olamines* in commercial applications. They are selected according to their relative ability to interact with and remove carbon dioxide and/or hydrogen sulfide.

The chemistry can be represented by simple equations for low partial pressures of the acid gases:



At high acid gas partial pressure, the reactions will lead to the formation of other products:



The reaction is extremely fast, the absorption of hydrogen sulfide being limited only by mass transfer; this is not so for carbon dioxide.

Regeneration of the solution leads to near complete desorption of carbon dioxide and hydrogen sulfide. A comparison between monoethanolamine, diethanolamine, and diisopropanolamine shows that monoethanolamine is the cheapest of the three amines but shows the highest heat of reaction and corrosion; the reverse is true for diisopropanolamine.

The processes using ethanolamine and potassium phosphate are now widely used. The ethanolamine process, known as the *Girbotol* process, removes acid gases (hydrogen sulfide and carbon dioxide) from liquid hydrocarbon derivatives as well as from natural and from refinery gases. The Girbotol process uses an aqueous solution of ethanolamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) that reacts with hydrogen sulfide at low temperatures and releases hydrogen sulfide at high temperatures. The ethanolamine solution fills a tower called an absorber through which the sour gas is bubbled. Purified gas leaves the top of the tower, and the ethanolamine solution leaves the bottom of the tower with the absorbed acid gases. The ethanolamine solution enters a reactivator tower where heat drives the acid gases from the solution. Ethanolamine solution, restored to its original condition, leaves the bottom of the reactivator tower to go to the top of the absorber tower, and acid gases are released from the top of the reactivator.

As currently practiced, acid gas removal processes involve the chemical reaction of the acid gases with a solid oxide (such as iron oxide) or selective absorption of the contaminants into a liquid (such as ethanolamine) that is passed countercurrent to the gas. Then, the absorbent is stripped of the gas components (regeneration) and recycled to the absorber. The process design will vary and, in practice, may employ multiple absorption columns and multiple regeneration columns.

Amine (olamine) washing of natural gas involves chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat, and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) have been used in commercial applications.

Processes that use methyl diethanolamine (MDEA) became popular with the natural gas industry because of its high selectivity for hydrogen sulfide over carbon dioxide. This high selectivity allows for a reduced solvent circulation rate, as well as a richer hydrogen sulfide feed to the sulfur recovery unit. The reaction of methyl diethanolamine with hydrogen sulfide is almost instantaneous. However, the reaction of methyl diethanolamine with carbon dioxide is much slower; the reaction rate of methyl diethanolamine with carbon dioxide is slower than that of carbon dioxide with ethanolamine.

Depending upon the application, special solutions such as mixtures of amines; amines with physical solvents such as sulfolane and piperazine; and amines that have been partially neutralized with an acid such as phosphoric acid may also be used.

A series of chemical activators used with methyl diethanolamine offers the most cost-effective answer to complete or controlled acid gas removal from sour to very sour natural gases. However, there are limitations of even the most advanced *activated methyl diethanolamine* only-based gas treatment technologies in handling very highly acid gas loaded natural or associated oil field gases, especially for bulk acid gas removal when the acid gases are destined for cycling and/or disposal by re-injection. The activated methyl diethanolamine process is a cost-effective solution that is available to meet the widest range of applications from complete carbon dioxide removal to bulk hydrogen sulfide and/or carbon dioxide removal even for acid gas re-injection projects.

See also: Gas Cleaning.

Olefin Hydrocarbons

Unsaturated (lower ratio of hydrogen to carbon) compounds of carbon and hydrogen having at least one double bond. The presence of the double bond renders the alkene much more reactive than the corresponding alkane (Table O-3).

Table O-3 Reactions of olefin derivatives (alkenes).

Reaction name 	Product 	Comment
Hydrogenation	alkanes	addition of hydrogen
Halogen addition	1,2-dihalide	electrophilic addition of halogens
Hydrohalogenation	haloalkanes	addition of hydrohalic acids
Hydroamination	amines	addition of N-H bond
Hydroformylation	aldehydes	addition of CO and H ₂
Bishydroxylation	diols	oxidation, reagent: osmium tetroxide
Cis-hydroxylation	diols	oxidation, reagents: iodine, silver acetate
ozonolysis	aldehydes or ketones	reagent: ozone
Olefin metathesis	alkenes	two alkenes rearrange to form two new alkenes
Diels-Alder reaction	cyclohexenes	cycloaddition with a diene
Hydroboration-oxidation	alcohols	reagents: borane, then a peroxide
oxymercuration-reduction	alcohols	electrophilic addition of mercuric acetate, then reduction
Prins reaction	1,3-diols	electrophilic addition with aldehyde or ketone
Paterno-Büchi reaction	oxetanes	photochemical reaction with aldehyde or ketone
Epoxidation	epoxide	electrophilic addition of an peroxide
Cyclopropanation	cyclopropanes	addition of carbenes or carbenoids

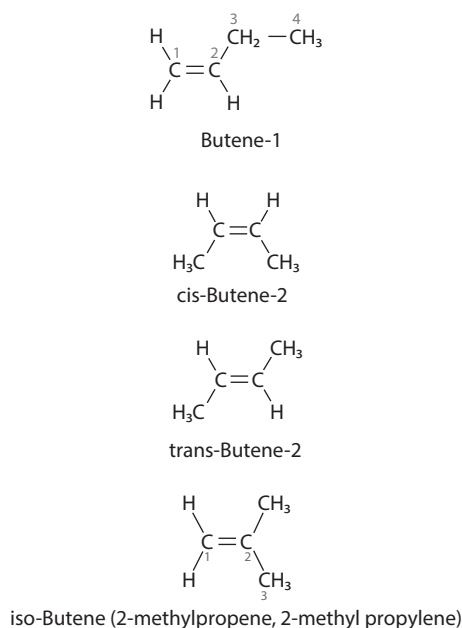
Refinery gas streams also contain olefin constituents that are produced by various cracking processes, and some streams also contain varying amounts of other chemicals including, ammonia, hydrogen, nitrogen, hydrogen sulfide, mercaptan derivatives, carbon monoxide, carbon dioxide, 1,3-butadiene, and/or benzene.

Some gases may also contain inorganic compounds, such as hydrogen, nitrogen, hydrogen sulfide, carbon monoxide, and carbon dioxide. Many low-molecular-weight olefins (such as ethylene and propylene) and diolefins (such as butadiene) which are produced in the refinery are isolated for petrochemical use. The individual products are: (i) ethylene, (ii) propylene, and (iii) butadiene.

Ethylene (C₂H₄) is a normally gaseous olefinic compound having a boiling point of approximately -104°C (-155°F) which may be handled as a liquid at high pressure and low temperature. Ethylene is made normally by cracking an ethane or naphtha feedstock in a high-temperature furnace and subsequent isolation from other components by distillation. The major uses of ethylene are in the production of ethylene oxide, ethylene dichloride, and the polyethylene polymers. Other uses include the coloring of fruit, rubber products, ethyl alcohol, and medicine (anesthetic).

Propylene concentrates are mixtures of propylene and other hydrocarbons, principally propane and trace quantities of ethylene, butylenes, and butanes. Propylene concentrates may vary in propylene content from 70% mol up to over 95% mol and may be handled as a liquid at normal temperatures and moderate pressures. Propylene concentrates are isolated from the furnace products mentioned in the preceding paragraph on ethylene. Higher purity propylene streams are further purified by distillation and extractive techniques. Propylene concentrates are used in the production of propylene oxide, isopropyl alcohol, polypropylene, and the synthesis of isoprene. As is the case for ethylene, moisture in propylene is critical.

Butylene concentrates are mixtures of butene-1, cis- and trans-butene-2, and, sometimes, isobutene (2-methyl propylene) (C₄H₈).



These products are stored as liquids at ambient temperatures and moderate pressures. Various impurities such as butane, butadiene, and the C_5 hydrocarbons are generally found in butylene concentrates. The majority of the butylene concentrates are used as a feedstock for either: (i) an alkylation plant, where isobutane and butylenes are reacted in the presence of either sulfuric acid or hydrofluoric acid to form a mixture of C_7 to C_9 paraffins used in gasoline, or (ii) butylene dehydrogenation reactors for butadiene production.

Butadiene (C_4H_6 , $CH_2=CHCH=CH_2$) is a normally gaseous hydrocarbon having a boiling point of -4.38°C (24.1°F) which may be handled as a liquid at moderate pressure. Ambient temperatures are generally used for long-term storage due to the easy formation of butadiene dimer (4-vinyl cyclohexene-1). Butadiene is produced by two major methods: the catalytic dehydrogenation of butane or butylenes or both, and as a by-product from the production of ethylene. In either case, the butadiene must be isolated from other components by extractive distillation techniques and subsequent purification to polymerization-grade specifications by fractional distillation. The largest end use of butadiene is as a monomer for production of GR-S synthetic rubber. Butadiene is also chlorinated to form 2-chloro-butadiene (chloroprene) ($CH_2=CHCCl=CH_2$) that is a feedstock used to produce neoprene (a polychloroprene rubber).

The major quality criteria for butadiene are the various impurities that may affect the polymerization reactions for which butadiene is used. The gas chromatographic examination of butadiene (ASTM, 2017) can be employed to determine the gross purity as well as C_3 , C_4 , and C_5 impurities. Most of these hydrocarbons are innocuous to polymerization reactions, but some, such as butadiene-1,2 and pentadiene-1,4, are capable of polymer crosslinking.

Rotation around the carbon-carbon double bond ($-C=C-$) is restricted because it involves breaking the pi bond, which requires a large amount of energy. As a consequence, substituted alkenes may exist as one of two isomers: (1) a cis isomer and a trans isomer. For example, in cis-but-2-ene, the two methyl substituents face the same side of the double bond and in trans-but-2-ene, they face the opposite side; these two isomers are slightly different in their chemical and physical properties.

All the alkenes with 4 or more carbon atoms in them show *structural isomerism*. This means that there are two or more different structural formulae that can be drawn for each molecular formula. For example, with butene (C_4H_8), there are three structural isomers (Figure O-1):

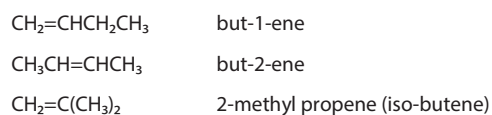


Figure O-1 Isomers of butene.

Butadiene (a diolefin, C_4H_6 , $CH_2=CHCH=CH_2$) is a normally gaseous hydrocarbon having a boiling point of $-4.38^\circ C$ ($24.1^\circ F$) which may be handled as a liquid at moderate pressure. Ambient temperatures are generally used for long-term storage due to the easy formation of butadiene dimer (4-vinyl cyclohexene-1). Butadiene is produced by two major methods: the catalytic dehydrogenation of butane or butylenes or both, and as a by-product from the production of ethylene. In either case, the butadiene must be isolated from other components by extractive distillation techniques and subsequent purification to polymerization-grade specifications by fractional distillation. The largest end use of butadiene is as a monomer for production of GR-S synthetic rubber. Butadiene is also chlorinated to form 2-chloro-butadiene (chloroprene) ($CH_2=CHCCl=CH_2$) that is a feedstock used to produce neoprene (a polychloroprene rubber).

The major quality criteria for butadiene are the various impurities that may affect the polymerization reactions for which butadiene is used. The gas chromatographic examination of butadiene (ASTM, 2017) can be employed to determine the gross purity as well as C_3 , C_4 , and C , impurities. Most of these hydrocarbons are innocuous to polymerization reactions, but some, such as butadiene-1,2 and pentadiene-1,4, are capable of polymer cross-linking.

See also: Alkanes, Alkenes, Refinery Gas.

Open Core Gasifier

The open core gasifier is a recent development of gasifier design for gasification of small-sized biomass with high ash content.

In the open core gasifier, the air is sucked over the whole cross section from the top of the bed. This facilitates better oxygen distribution since the oxygen will be consumed over the whole cross section, so that the solid bed temperature will not reach the local extremes (hot spots) observed in the oxidation zone of conventional gasifiers due to poor heat transfer. Moreover, the air nozzles in conventional gasifiers generate caves and create obstacles that may obstruct solid flow especially for solids of low bulk like rice husk.

On the other hand, the entry of air through the top of the bed creates a downward flow of the pyrolysis gases, and transports the tars products to the combustion zone. Thus, flow problems due to the caking of rice husk caused by back mixing of tar are avoided.

See also: Gasification, Gasification of Biomass.

Open-Loop Biomass

Open-loop biomass is biomass (such as cellulosic and lignin waste material) that can be used to produce energy and bioproducts even though it was not grown specifically for this purpose; includes agricultural livestock waste, residues from forest-harvesting, and crop-harvesting operations.

See also: Biomass, Cellulose, Lignin, Lignocellulose.

Organic Chemicals

The term organic chemicals includes a broad class of substances containing carbon and its derivatives. Many of these chemicals will frequently contain hydrogen with or without oxygen, nitrogen, sulfur, phosphorus, and other elements. They exist either in the form of a carbon chain or in the form of a carbon ring.

More specifically, organic chemicals are structurally diverse, and the range of application of organic chemicals is enormous. In addition, organic chemicals may contain any number of other elements, including nitrogen, oxygen, sulfur, halogens, phosphorus, and silicon. They form the basis of, or are important constituents of, many products (such as plastics, drugs, petrochemicals, food, explosives, and paints) and, with very few exceptions, they form the basis of all life processes and many industrial processes.

Organic compounds – of which the hydrocarbon derivatives are a sub-group – are classified according to the presence of functional groups in the molecule. A functional group is a molecular moiety that typically dictates the

behavior (reactivity) of the organic compound in the environment, and the reactivity of that functional group is assumed to be the same in a variety of molecules, within some limits and if steric effects (that arise from the three-dimensional structure of the molecule) do not interfere. Thus, most organic functional groups feature heteroatoms (atoms other than carbon and hydrogen, such as: nitrogen, oxygen, and sulfur). The concept of functional groups is major concept in organic chemistry, both to classify the structure of organic compounds and to predict the physical and chemical properties, especially, in the context of this book, those properties that relate to behavior and reactivity in technological processes.

Organic chemicals, from simple compounds such as methane (CH_4), to organic chemicals that contain more than one carbon atom, as many as ten carbon atoms to chemicals that contain hundreds or more carbon atoms that are linked in carbon-carbon bonds. Those that contain only carbon and hydrogen are called hydrocarbons; a simple example is $\text{H}_3\text{C}(\text{CH}_2)_3\text{CH}_3$ (pentane). Organic chemicals commonly contain other elements too, such as oxygen, nitrogen, or sulfur. An organometallic chemical has a carbon atom bonded to a metal as in tetraethyl lead. Some organometallic chemicals are found naturally.

Many organic chemicals are synthetic, i.e., produced not by living creatures, but manufactured by human beings. However, the feedstocks from which the chemicals are made come from nature. Commonly synthetic organic chemicals are made from crude oil or natural gas feedstocks, which are referred to as petrochemicals. Coal or wood also sometimes serves as feedstocks for organic chemicals. Plastics are synthetic organic chemicals, and the so-called bioplastics, which humans produce from plant materials, involve some synthetic chemistry. Some commercial organic chemicals are produced too by cultures of molds or bacteria; such chemicals must then be purified from these cultures by human actions.

Finally, for clarification, a biochemical is an organic chemical synthesized by a living creature. Proteins, fats, and carbohydrates are biochemicals. Sucrose (table sugar) and the acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) in vinegar are examples of simple biochemicals. Many biochemicals can also be made synthetically, not only simple chemicals such as vinegar or the sugars, sucrose, and xylose, but also complex ones. If the structure of a chemical made by synthetic means is exactly the same as that found in nature, it is indeed the same chemical – the body treats both in exactly the same way, so there is no biological difference between them. Chemicals synthesized by living creatures can also be extensively manipulated during extraction and purification and still legally be called natural.

See also: Inorganic Chemicals, Inorganic Matter, Organic Matter.

Organic Chemical Transformation Reactions

Reactions are chemical reactions involving compounds, and the basic chemical reaction types are (i) addition reactions, (ii) elimination reactions, (iii) substitution reactions, (iv) organic redox reactions, and (v) rearrangement reactions. In synthesis, reactions are used in the construction of new molecules, but in the discipline known as environmental chemistry, these reactions often occur and cause the chemical transformation of a pollutant in the environment. Factors governing reactions (hence, transformations) in the environment are essentially the same as that of any chemical reaction, and these are factors that determine the stability of reactants and products.

Furthermore, while organic reactions can be organized into several basic reaction types, some reactions fit into more than one category. Reactions can also be categorized on the basis of the type of functional group involved in the reaction as a reactant and the functional group that is formed as a result of this reaction. A functional group confers specific reactivity patterns on the molecules of which it is a part. Although the properties of each of the several million molecules whose structure is known are unique in some way, all molecules that contain the same functional group have a similar pattern of reactivity at the functional group site. Thus, functional groups are a key organizing feature of chemistry. By focusing on the functional groups present in a molecule (most molecules have more than one functional group), several of the reactions that the molecule will undergo can be predicted and understood. Thus, functional group transformation/interconversion is the process of converting one functional group into another functional group by any one (or more) of several reactions such as (i) substitution, (ii) addition, (iii) elimination, (iv) reduction, or (v) oxidation by the use of reagents under different reaction conditions.

In fact, there is no limit to the number of possible reactions and mechanisms. However, certain general patterns are observed that can be used to describe many common or useful reactions. Each reaction typically has a stepwise reaction mechanism that can be used to explain or visualize the mean by which the reaction occurs, although a detailed description of steps may not always be evident from a list of reactants alone.

Organic Chemical Transformation Reactions – Addition and Elimination Reactions

An addition reaction is an organic reaction where two or more molecules combine to form a product (the adduct) (March, 1992; Morrison *et al.*, 1992). Addition reactions are limited to chemical compounds that have multiple bonds, such as molecules with carbon-carbon double bonds (alkenes, $>C=C<$), or with triple bonds (alkynes, $-C\equiv C-$). Molecules containing carbon-heteroatom double bonds such as the carbonyl group ($>C=O$) groups, or the imine group ($C=N$) groups, can also participate in addition since they also have double bond character. An addition reaction is the reverse of an elimination reaction, such as the hydration of an alkene to an alcohol which is reversed by dehydration:



The main driver behind addition reactions to alkene is that alkenes contain the unsaturated $>C=C<$ functional group which characteristically undergoes addition reactions which is the conversion of the weaker π bond into two new, stronger σ bonds. In addition to addition reactions being typical of the unsaturated hydrocarbon derivatives (alkenes and alkynes) and aldehydes and ketones, which have a carbon-to-oxygen double bond. An addition reaction may be visualized as a process by which the double or triple bonds are fully or partially broken in order to accommodate additional atoms or groups of atoms in the molecule. Addition reactions to alkenes and alkynes are sometimes called saturation reactions because the reaction causes the carbon atoms to become saturated with the maximum number of attached groups.

In addition, reactions to aldehydes and ketones, the sequence of events is reversed insofar as the initial step is addition of the negatively charged component of the reagent to the carbon atom, followed by addition of the positively charged component to the oxygen atom.

Organic Chemical Transformation Reactions – Hydrolysis Reactions

Many compounds can be altered by a direct reaction of the chemical with water (hydrolysis) in which a chemical bond is cleaved and two new bonds are formed, each one having either the hydrogen component (H) or the hydroxyl component (OH) of the water molecule. Typically, the hydroxyl replaces another chemical group on the molecule and hydrolysis reactions are usually catalyzed by hydrogen ions or hydroxyl ions. This produces the strong dependence on the acidity or alkalinity (pH) of the solution often observed but, in some cases, hydrolysis can occur in a neutral (pH = 7) environment. Adsorption on to a mineral sediment (such as a clay sediment that has strong adsorptive powers) generally reduces the rates of hydrolysis for acid- or base-catalyzed reactions. Neutral reactions appear to be unaffected by adsorption, although there is always the possibility that the mineral sediment can cause catalyzed chemical transformation reactions.

The rate of a hydrolysis reaction is typically expressed in terms of the acid-catalyzed, neutral-catalyzed, and base-catalyzed hydrolysis rate constants. Furthermore, the hydrolysis of compounds is influenced by the composition of the solvent and the rate constants may be much higher in water than in solvents. In fact, the introduction of a complex mixture of chemicals into a water body can be expected to produce a significant shift in acidity or alkalinity of the medium and, therefore, it would not be surprising to anticipate that hydrolysis would be affected in complex mixtures.

Organic Chemical Transformation Reactions – Photolysis Reactions

Photolysis is a chemical process by which chemical bonds are broken as the result of transfer of light energy (direct photolysis) or radiant energy (indirect photolysis) to these bonds. The rate of photolysis depends upon numerous chemical and environmental factors including the light adsorption properties and reactivity of the chemical, and the intensity of solar radiation.

In the process, the photochemical mechanism of photolysis is divided into three stages: (i) the adsorption of light which excites electrons in the molecule, (ii) the primary photochemical processes which transform or de-excite the excited molecule, and (iii) the secondary thermal reactions which transform the intermediates produced in the previous step.

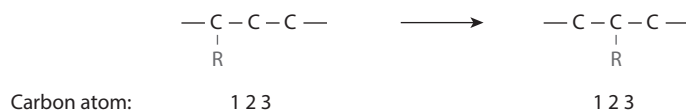
In addition, before photolysis can occur, the photochemically-excited state must be deactivated, such as a radiative process (fluorescence) in which energy (usually in the form of light) is emitted during the transition to ground electronic state and some residual vibrational excitation is rapidly lost via collision processes. Quenching of a photochemical process occurs when the excitation energy in the target molecule is transferred to some other chemical species in solution. This process results in net deactivation of the substance of concern via energy transfer.

Indirect photolysis or sensitized photolysis occurs when the light energy captured (absorbed) by one molecule is transferred to the molecule of concern. The donor species (the sensitizer) undergoes no net reaction in the process but has an essentially catalytic effect. Moreover, the probability of a sensitized molecule donating its energy to an acceptor molecule is proportional to the concentration of both chemical species. Thus, complex mixtures may, in some cases, produce enhancement of photolysis rates of individual constituents through sensitized reactions.

Organic Chemical Transformation Reactions – Rearrangement Reactions

Reactions typically yield products that are in accordance with the generally-accepted mechanism of the reactions. However, in some instances, reactions do not give exclusively and solely the anticipated products but may lead to other product that arises from unexpected and mechanistically different reaction path. This unexpected product is often referred to as a rearranged product and, while such a product may not be the expected product, it may be the major product of the reaction. Thus, the reaction has involved a rearrangement of the expected product to an unexpected product – a rearrangement reaction has occurred. More than likely, this may have resulted from a plausible rearrangement occurring during the mechanistic course of the reaction to fulfill the principle of the minimum energy state of the whole system, that is, of the transition state which assumed another configuration to maintain a minimum energy balance to the system. In many cases, the rearrangement affords products of an isomerization, coupled with some stereochemical changes. An energetic requirement is also observed in order for a rearrangement to take place; that is, the rearrangement usually involves an evolution of energy (typically in the form of heat, i.e., the reaction is overall an exothermic reaction) to be able to yield a more stable compound (Moulay, 2002).

Thus, a rearrangement reaction falls into a class of reactions where the carbon skeleton of an molecule is rearranged to form a structural isomer of the original molecule that assumes the minimal energy content of the product – i.e., the most stable product is formed (March, 1992; Morrison *et al.*, 1992; Moulay, 2002). As a result of the reaction, a substituent group typically moves from one atom to another atom in the same molecule to yield an isomer of the original reactant:



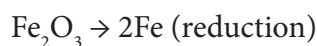
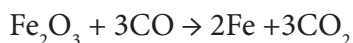
In the above equation, there has been movement of the substituents group (represented by R) from carbon atom number 1 to carbon atom number 2.

Thus, a rearrangement reaction is a reaction in which an atom or a group (or in some cases a bond) is caused to move or migrate to another part of the molecule. The reaction may involve several steps, but the defining feature is that the atom or a group or the bond shifts from one site of attachment to another site. The simplest (perhaps, the

most common) types of rearrangement reactions are intramolecular rearrangements insofar as the reactions occur in within one reactant molecule and the product of the reaction is a structural isomer of the reactant (Moulay, 2002).

Organic Chemical Transformation Reactions – Redox Reactions

Redox reactions (reduction-oxidation reactions) are reactions in which one chemical undergoes reduction and another chemical undergoes oxidation. Therefore, the oxidation state of the species involved must change. The word *reduction* originally referred to the loss in weight upon heating a metallic ore such as a metal oxide to extract the metal – the ore was *reduced* to the metal. However, the meaning of *reduction* has become generalized to include all processes involving gain of electrons. The term *hydrogenation* could be used instead of *reduction*, since hydrogen is the reducing agent in a large number of reactions, especially in chemistry and biochemistry. But, unlike oxidation, hydrogenation has maintained its specific connection to reactions that *add* hydrogen to another substance such as the hydrogenation processes used in a crude oil refinery. On the other hand, the word *oxidation* originally implied reaction with oxygen to form an oxide but the word has been expanded to encompass oxygen-like substances that accomplished parallel chemical reactions and ultimately, the meaning was generalized to include all processes involving loss of electrons. For example, the production of iron from the iron oxide ore:



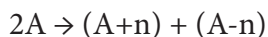
Similarly, in the context of chemistry, there is the oxidation of ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) to acetaldehyde (CH_3CHO) and the reverse reaction in which acetaldehyde is reduces to ethyl alcohol:



This equation can be sub-divided as follows into oxidation by loss of hydrogen and reduction by gain of hydrogen. Thus:



The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is the **oxidizing agent** which, by accepting electrons, causes the oxidation of another species. Conversely, the species that donates electrons is the **reducing agent** which, when the reaction occurs, reduces the other species. Thus, the species that is oxidized is the reducing agent and the species that is reduced is the oxidizing agent. To complicate matters even further, the oxidizing and reducing agents can be the same element or compound, as is the case when disproportionation of the reactive species occurs. For example:

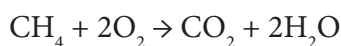


In this equation, n is the number of electrons transferred. Disproportionation reactions do not need to commence with a neutral molecule and can involve more than two species with differing oxidation states.

Redox reactions are important for a number of applications, including energy storage devices (batteries), photographic processing, and energy production and utilization in living systems including humans. For example, a *reduction reaction* is a reaction in which an atom gains an electron and therefore decreases (or reduces its oxidation

number). The result is that the positive character of the species is reduced. On the other hand, an oxidation reaction is a reaction in which an atom loses an electron and therefore increases its oxidation number. The result is that the positive character of the species is increased.

Although oxidation reactions are commonly associated with the formation of oxides from oxygen molecules, these are only specific examples of a more general concept of reactions involving electron transfer. Redox reactions are a matched set, that is, there cannot be an oxidation reaction without a reduction reaction happening simultaneously. The oxidation reaction and the reduction reaction always occur together to form a whole reaction. Although oxidation and reduction properly refer to a *change in the oxidation state*, the actual transfer of electrons may never occur. The oxidation state of an atom is the fictitious charge that an atom would have if all bonds between atoms of different elements were 100% ionic. Thus, oxidation is best defined as an *increase in oxidation state*, and reduction as a *decrease in oxidation state*. In practice, the transfer of electrons will always cause a change in oxidation state, but there are many reactions that are classed as redox reactions even though no electron transfer occurs (such as those involving covalent bonds). There are simple redox processes, such as the oxidation of carbon to carbon dioxide (CO₂) or the reduction of carbon by hydrogen to methane (CH₄).

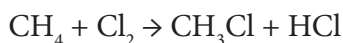


The key to identifying oxidation-reduction reactions is recognizing when a chemical reaction leads to a change in the oxidation number of one or more atoms.

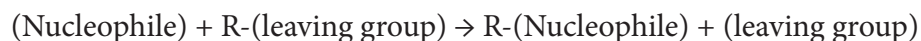
Organic Chemical Transformation Reactions – Substitution Reactions

A substitution reaction (sometimes referred to as a single displacement reaction or single replacement reaction) is a reaction in which a functional group in an organic chemical is replaced by another functional group (March, 1992; Morrison *et al.*, 1992). Substitution reactions are of prime importance in environmental organic chemistry because of the simplicity of the reaction which is accompanied by a substantial change in the chemical and physical properties of the product vis-à-vis compared to the chemical and physical properties of the starting chemical. Substitution reactions in organic chemistry are classified either as (i) nucleophilic substitution or (ii) electrophilic substitution depending upon the reagent involved.

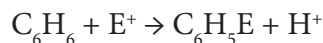
A nucleophile is a chemical species (an ion or a molecule) which is strongly attracted to a region of positive charge in something else. Nucleophiles are either fully negative ions, or else have a strongly (δ-) charge somewhere on a molecule. Common nucleophiles are hydroxide ions (OH⁻), cyanide ions (CN⁻), water (H₂O), and ammonia (NH₃). An example of a simple nucleophilic substitution reaction is the halogenation of an alkane such as when methane (CH₄) is reacted with chlorine (Cl₂) to form methyl chloride and hydrogen chloride:



Thus, a nucleophilic substitution reaction (which is common in organic chemistry) is a reaction in which an electron-rich nucleophile selectively bonds with or attacks the positive or partially positive charge of an atom or a group of atoms to replace the leaving electrophile:



On the other hand, electrophilic substitution involves electrophiles, and an example is electrophilic aromatic substitution. In this type of substitution, the benzene ring (which has a π-electron cloud above and below the plane of the ring of carbon atoms) is attacked by an electrophile (shown as E⁺). The π-electron cloud is disturbed, and a carbocation resonating structure results after which a proton (H⁺) is ejected from the intermediate and a new aromatic compound is formed:



A relevant reaction in the environment (because of the ever-presence of water in many ecosystems) is the hydrolysis reaction in which a chemical compound is decomposed by reaction with water – also, the hydrolysis reaction should not be confused with the *hydrogenolysis* reaction which is a reaction of hydrogen as practiced widely in the crude oil industry to produce liquid fuels. Hydrolysis is an example of a larger class of reactions referred to as nucleophilic displacement reactions in which a nucleophile (an electron-rich species containing an unshared pair of electrons) attacks an electrophilic atom (an electron-deficient reaction center). Hydrolytic processes encompass several types of reaction mechanisms that can be defined by the type of reaction center (i.e., the atom bearing the leaving group, X) where hydrolysis occurs. The reaction mechanisms encountered most often are direct and indirect nucleophilic substitution and nucleophilic addition-elimination.

This type of reaction can be used to predict the persistency of a chemical in the environment, the physical-chemical properties of the chemical, and the reactivity of the chemical in the environment need to be known or at least estimated (Rahm *et al.*, 2005). The chemicals that can undergo elimination reactions are rapidly transformed, as are perhalogenated chemicals that can undergo substitution reactions. These chemicals are not likely to persist in the environment, while those that do not show any observable reactivity under similar hydrolytic conditions are likely to be persistent pollutants (POPs) and the fate of these chemicals is linked to the cycling of chemicals in the environment.

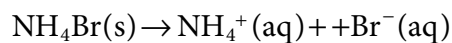
Typically, the hydrolysis reaction is a chemical transformation in which a molecule, RX, reacts with water, resulting in the formation of a new covalent bond with the hydroxy function (OH) and cleavage of the covalent bond with halogen function (e.g., Cl) (the leaving group) in the original molecule. The net reaction is the displacement of the halogen group (X) by the hydroxyl group (OH). In fact, for many types of contaminants, hydrolysis may be the dominant pathway for their transformation in aquatic ecosystems. Hydrolytic processes are not limited to the bodies of water such as rivers, streams, lakes, and oceans usually associated with the term aquatic ecosystems. Hydrolysis of chemicals can also occur in groundwater systems and the aqueous environment in solids and sediments.

In the aqueous hydrolysis reaction, the reacting water molecules are split into hydrogen (H^+) and hydroxide (OH^-) ions, which react with and break up the other reacting compound. The term *hydrolysis* is also applied to the electrolysis of water (that is, breaking up of water molecules by an electric current) to produce hydrogen and oxygen. The hydrolysis reaction is distinct from a *hydration reaction*, in which water molecules attach to molecules of the other reacting compound without breaking up the latter compound, such as:



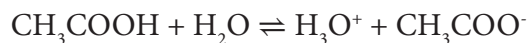
The hydrolysis reaction mainly occurs between an ion and water molecules and often changes the pH (acidity or alkalinity) of a solution. In chemistry, there are three main types of hydrolysis (i) salt hydrolysis, (ii) acid hydrolysis, and (iii) base hydrolysis.

In water, salts will dissociate to form ions (either completely or incompletely depending on the respective solubility constant, K_{sp}). For example:



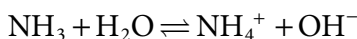
In this equation, the salt (ammonium bromide, NH_4Br) is dissolved in water upon which the salt dissociates into ammonium ions (NH_4^+) and bromide ions (Br^-).

In the hydrolysis reaction, water can act as an acid or a base: (i) if that water acts as an acid, the water molecule would donate a proton (H^+), also written as a hydronium ion (H_3O^+) or (ii) if the water acts as a base, the water molecule would accept a proton (H^+). An acid hydrolysis reaction is very much the same as an acid dissociation reaction.



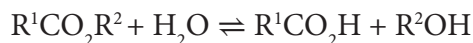
In the above reaction, the proton H^+ from CH_3COOH (acetic acid) is donated to water, producing the hydronium ion (H_3O^+) and an acetate ion (CH_3COO^-). The bonds between proton and the acetate ion are dissociated by the addition of water molecules. A reaction with acetic acid (CH_3COOH), a weak acid, is similar to an acid-dissociation reaction, and water forms a conjugate base and a hydronium ion. When a weak acid is hydrolyzed, a hydronium ion is produced.

A base hydrolysis reaction will resemble the reaction for base dissociation. A common weak base that dissociates in water is ammonia:

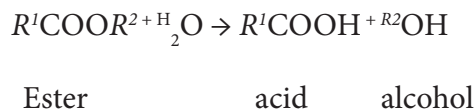


In the hydrolysis of ammonia, the ammonia molecule accepts a proton from the water (i.e., water acts as an acid), producing a hydroxide anion (OH^-). Similar to a basic dissociation reaction, ammonia forms ammonium and a hydroxide from the addition of a water molecule.

Generally, in chemistry, hydrolysis can be considered the reverse (or opposite) of condensation, a reaction in which two molecular fragments are joined for each water molecule produced. Since hydrolysis may be a reversible reaction, condensation and hydrolysis can take place at the same time, with the position of equilibrium determining the amount of each product, such as the hydrolysis of an ester to an acid and an alcohol:



Thus, hydrolysis reactions involving compounds may be illustrated by the reaction of water with an ester of a carboxylic acid; all such esters have the general formula R^1COOR^2 , in which R^1 and R^2 are combining groups (for example, if R^1 and R^2 are both methyl groups, CH_3 , the ester is methyl acetate). The hydrolysis involves several steps, of which the slowest is the formation of a covalent bond between the oxygen atom of the water molecule and the carbon atom of the ester. In succeeding steps, which are very rapid, the carbon-oxygen bond of the ester breaks and hydrogen ions become detached from the original water molecule and attached to the nascent alcohol molecule. The whole reaction is represented by the equation:

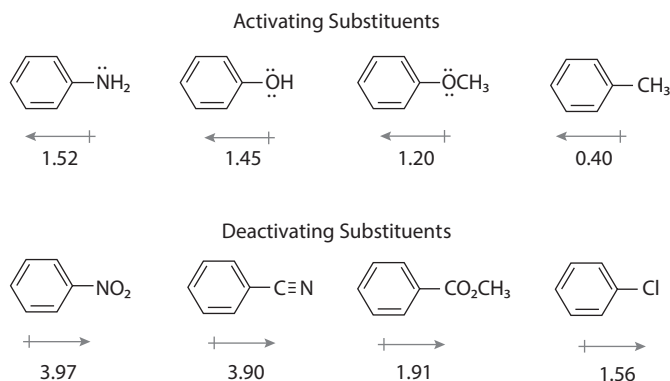


Thus, the products of hydrolysis depend very much upon that substrate that is to be hydrolyzed.

More pertinent to the present text, the hydrolysis of a pesticide is basically a reaction with a water molecule involving specific catalysis by proton or hydroxide, and sometimes in ions such as phosphate ion, present in the aquatic environment that play a role in general acid-base catalysis (Katagi, 2002). However, the hydrolytic profiles depend on the chemical structure and functional group(s) in the pesticide molecule, which are not always consistent within a chemical class of pesticides (Stoytcheva, 2011). For example, pesticides that are composed of organophosphorus derivatives are primarily susceptible to alkaline hydrolysis with less acidic catalysis, but some of phosphorodithioate derivatives are found to be acid labile. Various instrumental techniques have been applied to chemical identification of degraded products, leading to clarification of the reaction mechanisms involved. Moreover, pesticides are usually applied as a suitable formulation, and thus the effects of surfactants and other formulation reagents on hydrolysis should be examined in more detail. To assess the fate and impact of pesticides and their degraded products in real aquatic environments, these concerns should be further examined using the various analytical techniques together with simulation models.

When substituted benzene compounds undergo electrophilic substitution reactions, it is necessary to compare the relative reactivity of the compound compared with benzene itself. Experiments have shown that substituents on a benzene ring can influence reactivity in a profound manner. For example, a hydroxy substituent ($-OH$) or methoxy ($-OCH_3$) substituent increases the rate of electrophilic substitution approximately ten thousand-fold. In contrast, a nitro substituent decreases the reactivity of the ring substantially. This **activation or deactivation** of the benzene

ring toward electrophilic substitution may be correlated with the electron-donating or electron-withdrawing influence of the substituents, as measured by molecular dipole moments. Electron-donating substituents activate the benzene ring toward electrophilic attack, and electron-withdrawing substituents deactivate the benzene ring and render it less reactive to electrophilic attack.



The influence a substituent exerts on the reactivity of a benzene ring may be explained by the interaction of two effects: (i) an inductive effect, and (ii) a conjugative effect. The *inductive effect* arises because most elements other than metals and carbon have a significantly greater electronegativity than hydrogen. Consequently, substituents in which nitrogen, oxygen, and halogen atoms form sigma-bonds to the aromatic ring exert an inductive electron withdrawal, which deactivates the ring (left-hand diagram below). The second effect (the conjugative effect) is the result of a conjugation of a substituent function with the aromatic ring which facilitates electron pair donation or withdrawal, to or from the benzene ring, in a manner different from the inductive shift. If the atom bonded to the ring has one or more non-bonding valence shell electron pairs, as do nitrogen, oxygen, and the halogens, electrons may flow into the aromatic ring by π conjugation (resonance), as in the middle diagram. Finally, polar double and triple bonds conjugated with the benzene ring may withdraw electrons, as in the right-hand diagram. The charge distribution in the benzene ring is greatest at sites ortho and para to the substituent. In the case of the nitrogen- and oxygen-activating groups displayed in the top row of the previous diagram, electron donation by resonance dominates the inductive effect and these compounds show exceptional reactivity in electrophilic substitution reactions. Although halogen atoms have non-bonding valence electron pairs that participate in p - π conjugation, their strong inductive effect predominates, and compounds such as chlorobenzene are less reactive than benzene.

Organic Matter

The organic material of soil, called humus, is made up of microorganisms (dead and alive), and dead animals and plants in varying stages of decay. Humus improves soil structure, providing plants with water and minerals

The solid fraction of typical productive soil is ca. 5% w/w organic matter and ca. 95% w/w inorganic matter. Some soils, such as peat soils, may contain as much as 95 % organic material. Other soils contain as little as 1% w/w organic matter. Though typically comprising less than 5% w/w of a productive soil, organic matter in soil largely determines soil productivity. It serves as a source of food for microorganisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil. Some organic compounds even contribute to the weathering of mineral matter, the process by which soil is formed.

Humus is a generic term for the water-insoluble material that makes up the bulk of soil organic matter (Stevenson, 1994). Humus is composed of a base-soluble fraction (humic and fulvic acids) and an insoluble fraction (humin) and is the residue from the biodegradation (by bacteria and fungi) of plant material. The bulk of plant biomass consists of relatively degradable cellulose and degradation-resistant lignin, a complex polymeric substance that is second only to carbohydrates in natural abundance. Lignin is a precursor of soil humus.

The accumulation of organic matter in soil is strongly influenced by temperature and by the availability of oxygen. Since the rate of biodegradation decreases with decreasing temperature, organic matter does not degrade rapidly in

colder climates and tends to build up in soil. In water and in waterlogged soils, decaying vegetation does not have easy access to oxygen, and organic matter accumulates. The organic content may reach 90% w/w in areas where plants grow and decay in soil saturated with water. Of the organic components, humus is by far the most significant.

An increase in the atomic nitrogen/carbon ratio is a significant feature of the transformation of plant biomass to humus. During the humification process, microorganisms convert organic carbon to carbon dioxide to obtain energy. Simultaneously, the bacterial action incorporates bound nitrogen with the compounds produced by the decay processes. The result is a nitrogen/carbon ratio of ca. 1/10 upon completion of humification. As a general rule, therefore, humus is relatively rich in organically bound nitrogen.

Humic materials in soil strongly adsorb many solutes in soil water and have a particular affinity for heavy polyvalent cations. Soil humic substances may contain levels of uranium more than 10,000 times that of the water with which they are in equilibrium. Thus, water becomes depleted of its cations (or purified) in passing through humic-rich soils. Humic substances in soils also have a strong affinity for organic compounds with low water solubility such as the types of herbicides widely used to kill weeds.

In some cases, there is a strong interaction between the organic and inorganic portions of soil. This is especially true of the strong complexes formed between clay minerals and humic (fulvic) acid compounds. In many soils, 50-100% of the soil carbon is in the form of complexes with clay. These complexes play a role in determining the physical properties of soil, soil fertility, and stabilization of soil organic matter. One of the mechanisms for the chemical binding between clay colloidal particles and humic organic particles are probably of the flocculation type, in which anionic organic molecules with carboxylic amid functional groups serve as bridges in combination with cations to bind clay colloidal particles together as a floe.

The synthesis, chemical reactions, and biodegradation of humic materials are affected by interaction with clay minerals. The lower-molecular-weight fulvic acids may be bound in the spaces in layers in clay particles.

See also: Inorganic Chemicals, Inorganic Matter, Organic chemicals.

Organic Solvents

Solvents are liquids or gases that can dissolve or extract other substances and are an essential part of laboratory operations – typically for use to dissolve substances or for cleaning – and must be used with caution. Solvents are used to dissolve materials such as grease, oil, and paint, to thin or mix pigments, paint, glue, and pesticides.

The term *solvents* usually refers to organic solvents, which contain carbon and can be classified into three main types: (i) hydrocarbon solvents, (ii) oxygenated solvents, and (iii) halogenated solvents. Hydrocarbon solvents contain hydrogen and are derived mainly from petroleum, while oxygenated solvents are synthesized from other chemicals. Halogenated solvents contain one or more of the halogen elements: chlorine, bromine, fluorine, or iodine.

In the interests of safety and health, the properties of any solvent must be determined before use.

Other Energy Resources

It is predictable that fossil fuels will be the primary source of energy for the next several decades, well into the next century, and therefore the message is clear: until other energy sources supplant coal, natural gas, and crude oil, the challenge is for the development of technological concepts that will provide the maximum recovery of energy from these fossil fuel resources. Thus, it is absolutely essential that energy from such resources be obtained not only cheaply but also efficiently and with minimal detriment to the environment.

To complete the energy resource scenario and to put the fossil energy resources into perspective, there are non-fossil fuel energy resources which are derived from the sun and are generically referred to as non-fossil resources, or renewable resources, or/and geophysical energy resources. And even though it is not widely recognized, since renewable energy resources are assumed to be “natural” and therefore in harmony with nature, there are environmental issues that need to be addressed when renewable energy resources are to be employed.

Beyond this, there is much doubt related to the time when humans can look forward to the generation of energy from the unconventional sources. The time scale for the generation of electrical energy from such sources is generally

unknown or, at best, open to much speculation and criticism. The resources include direct solar energy, hydroelectric energy, wind energy, geothermal energy, energy from biomass, and elements of minerals from which nuclear energy may be derived.

Nuclear energy, which can be as hazardous as any fossil fuel in terms of destruction of the environment, deserves some comment insofar as an appreciation of its use may assist in the general background and aid in putting fossil fuel resources into a more complete context. Energy from nuclear sources has shown potential to be a significant energy source in the future.

Energy from nuclear sources may be the result of nuclear fission, which uses uranium ore or refined uranium-235 as its basic energy source. The ore must be concentrated into fissionable isotopes through nuclear processing. Eventually, the spent material must be replaced, hence the need to explore the potential for generating more of the fissionable isotopes. However, the use of such materials has become the core of a major controversy which threatens to be, at least for the time being, the death-knell of the nuclear industry.

Nuclear fusion, unlike nuclear fission which involves the use of fissionable material, involves the fusion of hydrogen nuclei. The concept has been suggested as having the potential to provide a clean and virtually unlimited supply of energy.

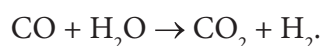
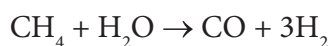
Oxidation

Oxidation is a process which can be used for the treatment of a variety of inorganic and organic substances.

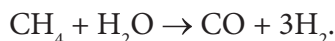
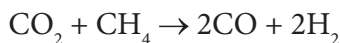
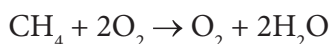
The oxidation of hydrocarbon derivatives and hydrocarbon mixtures has received considerable attention, but the uncontrollable nature of the reaction and the mixed character of the products have made resolution of the reaction sequences extremely difficult.

Therefore it is not surprising that, except for the preparation of mixed products having specific properties, such as fatty acids, hydrocarbon derivatives higher than pentanes are not employed for oxidation because of the difficulty of isolating individual compounds.

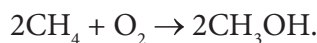
Methane undergoes two useful reactions at 90°C (195°F) in the presence of iron oxide (Fe_3O_4) as a catalyst:



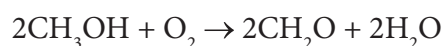
Alternatively, partial combustion of methane can be used to provide the required heat and steam. The carbon dioxide produced then reacts with methane at 900°C (1,650°F) in the presence of a nickel catalyst:



Methanol (methyl alcohol, CH_3OH) is the second major product produced from methane. Synthetic methanol has virtually completely replaced methanol obtained from the distillation of wood, its original source material. One of the older trivial names used for methanol was wood alcohol. The synthesis reaction takes place at 350°C (650°F) and 4,400 psi in the presence of ZnO as a catalyst:

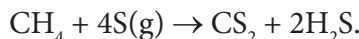


Most of the methanol is then oxidized by oxygen from air to formaldehyde (sometimes referred to as *methanal*):



Formaldehyde is used to produce synthetic resins either alone or with phenol, urea, or melamine; other uses are minor.

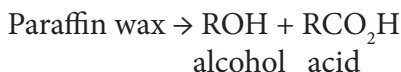
By analogy to the reaction with oxygen, methane reacts with sulfur in the presence of a catalyst to give the carbon disulfide used in the rayon industry:



When propane and butane are oxidized in the vapor phase, without a catalyst, at 270 to 350°C (520 to 660°F) and at 50 to 3,000 psi, a wide variety of products is obtained, including C₁ to C₄ acids, C₂ to C₇ ketones, ethylene oxide, esters, formals, acetals, and others.

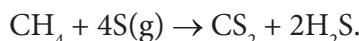
Cyclohexane is oxidized commercially and is somewhat selective in its reaction with air at 150 to 250°C (300 to 480°F) in the liquid phase in the presence of a catalyst, such as cobalt acetate. Cyclohexanol derivatives are the initial products, but prolonged oxidation produces adipic acid. On the other hand, oxidation of cyclohexane and methylcyclohexane over vanadium pentoxide at 450 to 500°C (840 to 930°F) affords maleic and glutaric acids.

The preparation of carboxylic acids from crude oil, particularly from paraffin wax, for esterification to fats or neutralization to form soaps has been the subject of a large number of investigations. Wax oxidation with air is comparatively slow at low temperature and normal pressure, little reaction taking place at 110°C (230°F), with a wax melting at 55°C (130°F) after 280 h. At higher temperatures, the oxidation proceeds more readily; maximum yields of mixed alcohol and high-molecular-weight acids are formed at 110 to 140°C (230 to 285°F) at 60 to 150 psi; higher temperatures (140 to 160°C, 285 to 320°F) result in more acid formation:



Acids from formic (HCO₂H) to that with a 10-carbon atom chain [CH₃(CH₂)₉CO₂H] have been identified as products of the oxidation of paraffin wax. Substantial quantities of water-insoluble acids are also produced by the oxidation of paraffin wax, but apart from determination of the average molecular weight (ca. 250), little has been done to identify individual numbers of the product mixture.

By analogy to the reaction with oxygen, methane reacts with sulfur in the presence of a catalyst to give the carbon disulfide used in the rayon industry:



The major non-petrochemical use of methane is in the production of hydrogen for use in the Haber synthesis of ammonia. Ammonia synthesis requires nitrogen, obtained from air, and hydrogen. The most common modern source of the hydrogen consumed in ammonia production, approximately 95% of it, is methane.

Oxygen

Oxygen occurs in both the organic and inorganic portions of coal. In the organic portion, oxygen is present in hydroxyl (-OH), usually phenol groups, carboxyl groups (CO₂H), methoxyl groups (-OCH₃), and carbonyl groups (=C=O). In low-rank coal, the hydroxyl oxygen averages approximately 6 to 9%, while high-rank coals contain less than 1%. The percentages of oxygen in carbonyl, methoxyl, and carboxyl groups average from a few percent in low rank and brown coal to almost no measurable value in high-rank coal. The inorganic materials in coal that contain oxygen are the various forms of moisture, silicates, carbonates, oxides, and sulfates. The silicates are primarily aluminum silicates found in the shale-like portions. Most of the carbonate is calcium carbonate (CaCO₃), the oxides are mainly iron oxides (FeO and Fe₂O₃), and the sulfates are calcium and iron (CaSO₄ and FeSO₄).

See also: Ozone.

Oxygenated Gasoline

Oxygenated gasoline is gasoline with added ethers or alcohols, formulated according to the Federal Clean Air Act to reduce carbon monoxide emissions during winter months.

See also: Oxygenates

Oxygenates

Oxygenates are chemical compounds which, when added to gasoline, increase the amount of oxygen in that gasoline blend; include fuel ethanol, methanol, and methyl-tertiary-butyl ether (MTBE).

Oxygenates are carbon-, hydrogen-, and oxygen-containing combustible liquids that are added to gasoline to improve performance. The addition of oxygenates gasoline is not new since ethanol (ethyl alcohol or grain alcohol) has been added to gasoline for decades. Thus, *oxygenated gasoline* is a mixture of conventional hydrocarbon-based gasoline and one or more oxygenates. The current oxygenates belong to one of two classes of organic molecules: alcohols and ethers. The most widely used oxygenates in the United States are ethanol, methyl tertiary-butyl ether (MTBE), and tertiary-amyl methyl ether (TAME). Ethyl tertiary-butyl ether (ETBE) is ether that could be used. Oxygenates may be used in areas of the United States where they are not required as long as concentration limits (as defined by environmental regulations) are observed.

Of all the oxygenates, methyl-t-butyl ether (MTBE) is attractive for a variety of technical reasons. It has a low vapor pressure, can be blended with other fuels without phase separation, and has the desirable octane characteristics. If oxygenates achieve recognition as vehicle fuels, the biggest contributor will probably be methanol, the production of which is mostly from synthesis gas derived from methane.

The higher alcohols also offer some potential as motor fuels. These alcohols can be produced at temperatures below 300°C (570°F) using copper oxide-zinc oxide-alumina catalysts promoted with potassium. Iso-butyl alcohol is of particular interest because of its high octane rating, which makes it desirable as a gasoline-blending agent. This alcohol can be reacted with methanol in the presence of a catalyst to produce methyl-t-butyl ether. Although it is currently cheaper to make iso-butyl alcohol from iso-butylene, it can be synthesized from syngas with alkali-promoted zinc oxide catalysts at temperatures above 400°C (750°F).

See also: Alcohols, Ethanol, Liquid Fuels, Methanol, Oxygenated Gasoline, Oxygenates.

Oxygen Compounds

Oxygen in organic compounds – especially organic compounds that are produced from the various types of biomass, such as bio-oil – can occur in a variety of forms (ROH , ArOH , R^1OR^2 , RCO_2H , ArCO_2H , RCO_2R , ArCO_2R , $\text{R}_2\text{C}=\text{O}$ as well as the cyclic furan derivatives, where R, R^1 , and R^2 are alkyl groups and Ar is an aromatic group) in nature, so it is not surprising that the more common oxygen-containing compounds occur in crude oil. The total oxygen content of crude oil is usually less than 2% w/w, although larger amounts have been reported, but when the oxygen content is phenomenally high, it may be that the oil has suffered prolonged exposure to the atmosphere either during or after production. However, the oxygen content of crude oil increases with the boiling point of the fractions examined; in fact, the nonvolatile residua may have oxygen contents up to 8% w/w. Although these high-molecular-weight compounds contain most of the oxygen in crude oil, little is known concerning their structure, but those of lower molecular weight have been investigated with considerably more success and have been shown to contain carboxylic acids and phenols.

The presence of acid substances in crude oil first appears to have been reported in 1874, and it was established 9 years later that these substances contained carboxyl groups and were carboxylic acids. These were termed naphthenic acids. Although alicyclic (naphthenic) acids appear to be the more prevalent, it is now well known that aliphatic acids are also present. In addition to the carboxylic acids, alkaline extracts from crude oil contain phenols.

It has generally been concluded that the carboxylic acids in crude oil with fewer than eight carbon atoms per molecule are almost entirely aliphatic in nature; monocyclic acids begin at C_6 and predominate above C_{14} . This indicates that the structures of the carboxylic acids correspond with those of the hydrocarbon derivatives with which they are associated in the crude oil. In the range in which paraffins are the prevailing type of hydrocarbon, the aliphatic acids may be expected to predominate. Similarly, in the ranges in which monocycloparaffin derivatives and dicycloparaffin derivatives prevail, one may expect to find principally monocyclic and dicyclic acids, respectively.

In addition to the carboxylic acids and phenolic compounds, the presence of ketones, esters, ethers, and anhydrides has been claimed for a variety of crude oils. However, the precise identification of these compounds is difficult because most of them occur in the higher-molecular-weight nonvolatile residua. They are claimed to be products of the air blowing of the residua, and their existence in virgin crude oil may yet need to be substantiated.

Although comparisons are frequently made between the sulfur and nitrogen contents and such physical properties as the API gravity, it is not the same with the oxygen contents of crude oils. It is possible to postulate, and show, that such relationships exist. However, the ease with which some of the crude oil constituents can react with oxygen (aerial or dissolved) to incorporate oxygen functions into their molecular structure often renders the exercise somewhat futile if meaningful deductions are to be made.

Oxygen Cycle

The oxygen cycle is the biogeochemical transitions of oxygen atoms between different oxidation states in ions, oxides, and molecules through redox reactions within and between the spheres and reservoirs of the planet Earth. The word redox typically refers to the most common oxygen allotrope, elemental/diatomic oxygen (O_2), as it is a common product or reactant of many biogeochemical redox reactions within the cycle. Processes within the oxygen cycle are considered to be biological or geological and are evaluated as either a source (oxygen production) or a sink (oxygen consumption).

In the oxygen cycle, the circulation of oxygen in various forms occurs in nature. Free in the air and dissolved in water, oxygen is second only to nitrogen in abundance among uncombined elements in the atmosphere. Plants and animals use oxygen to respire and return it to the air and water as carbon dioxide (CO_2) which is then taken up by algae and terrestrial green plants and converted into carbohydrates during the process of photosynthesis with oxygen being a by-product. The waters of the world are the main oxygen generators of the biosphere; their algae are estimated to replace approximately 90% of all oxygen used. Oxygen is involved to some degree in all the other biogeochemical cycles. For example, over time, detritus from living organisms transfers oxygen-containing compounds (such as calcium carbonate) into the lithosphere.

See also: Biogeochemical Cycles, Geological Cycles.

Oxygen Delignification

Oxygen delignification is primarily intended to facilitate the delignification process, i.e., bleaching. More effective delignification enables the process to reduce the use of hazardous and expensive chemicals in the bleach plant.

Oxygen delignification is a process between cooking and bleaching sequences, where part of the residual lignin left in pulp after cooking is removed using oxygen and alkali. Oxygen delignification is a direct extension to delignification in cooking. The targeted reactions are the oxidation of lignin and breaking it down to parts which dissolve in alkali, as well as destroying the colored groups in lignin and removal of impurities, such as resin.

In the process, oxygen is reduced to water in reactions with the organic components, and the organic components are oxidized. Oxygen in its normal state is a weak oxidizing agent, and is as such ineffective in delignification. Its oxidizing power can be promoted by raising the temperature and by alkaline conditions.

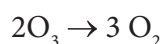
The most essential factor in oxygen delignification is to bring oxygen gas into contact with the fibers under alkaline conditions – the pulp suspension should have enough alkaline (hydroxyl ions) to neutralize and dissolve the organic acids, which are generated in oxygen-lignin reactions.

Oxygen delignification can be done in medium or high consistency. A high consistency oxygen stage is more expensive and more difficult to process than a medium consistency stage. Medium consistency oxygen delignification can be performed as a single- or two-stage system. The number of stages depends on the extent of the reaction required.

With the increasing importance of environmental conservation and the inevitable depletion of the fossil fuel supplies of the Earth, it is necessary to develop renewable and clean sources of energy. Bioconversion, the process of converting plant biomass to fuel-grade ethanol, is one process that addresses these concerns. However, despite promising results, the development of a more feasible pretreatment process to be used upstream of enzymatic hydrolysis is required. Oxygen delignification has long been successfully employed in the pulp and paper industry to remove the lignin from pulp samples.

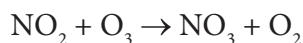
Ozone

Ozone (O_3) occurs naturally in the upper layers of the atmosphere. This important gas shields the earth from the harmful ultraviolet rays of the sun. However, at the ground level, it is a pollutant with highly toxic effects. **Ozone depletion** is another result of pollution. The ozone layer in the stratosphere protects the earth from harmful *ultraviolet radiation* from the sun. Release of *chlorofluorocarbons* (CFCs) from aerosol cans, cooling systems, and refrigerator equipment remove some of the ozone, causing “holes,” to open up in this layer and allowing the radiation to reach the earth. Ozone is a powerful oxidizing agent and unstable at high concentrations, decaying to ordinary diatomic oxygen (in approximately half an hour in atmospheric conditions):



This reaction proceeds more rapidly with increase in temperature and decrease in pressure.

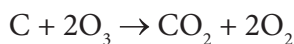
Ozone also increases the oxidation number of oxides, such as the oxidation of nitric oxide to nitrogen dioxide:



The NO_3 formed can react with NO_2 to form N_2O_5 :



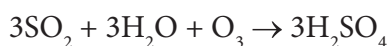
Ozone reacts with carbon to form carbon dioxide, even at room temperature:



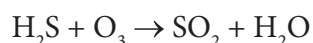
Ozone does react with ammonia to form ammonium nitrate:



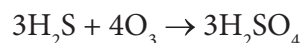
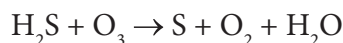
Sulfuric acid can be produced from ozone, starting either from elemental sulfur or from sulfur dioxide:



In the gas phase, ozone reacts with hydrogen sulfide to form sulfur dioxide:



In an aqueous solution, however, two competing simultaneous reactions occur, one to produce elemental sulfur, and one to produce sulfuric acid:



Nitryl perchlorate can be made from NO_2 , ClO_2 , and O_3 gases:

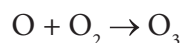
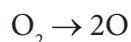


See also: Oxygen, Ozone Layer

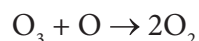
Ozone Layer

Ozone only makes up approximately 0.00006% of the atmosphere, and the highest levels of ozone in the atmosphere are in the *stratosphere*, in a region also known as the ozone layer between approximately 4 to 20 miles above the surface (or between approximately 6 and 31 miles). The ozone layer filters out photons with shorter wavelengths (less than 320 nm) of ultraviolet light (UV rays, 270 to 400 nm) from the Sun which, in large doses, would be harmful to most forms of life in large doses. These same wavelengths are also among those responsible for the production of vitamin D, a vitamin also produced by the human body.

Ozone in the stratosphere is mostly produced from ultraviolet rays reacting with oxygen:



Ozone is destroyed by the reaction with atomic oxygen:



The latter reaction is catalyzed by the presence of certain free radicals, of which the most important are hydroxyl (OH), nitric oxide (NO), atomic chlorine (Cl), and bromine (Br).

In recent decades – since the middle of the 20th century – there has been a noticeable decrease in the amount of ozone in the stratosphere mostly because of emissions of chlorofluorocarbons (CFCs) and similar chlorinated and brominated organic molecules, which have increased the concentration of ozone-depleting catalysts above the natural background.

See also: Atmosphere, Ozone.

Packed Bed

A packed bed – in the current context – is a hollow tube, pipe, or other vessel that is filled with a packing material such as a neutral non-reactive material to provide a large surface area or a catalyst. The packing can be randomly filled with small objects like Raschig rings, or else, it can be a specifically designed structured packing. Packed beds may also contain catalyst particles or adsorbents such as zeolite pellets or granular activated carbon.

The purpose of a packed bed is typically to improve contact between two phases in a chemical or similar process. Packed beds can be used in a chemical reactor, a distillation process, or a scrubber, but packed beds have also been used to store heat in chemical plants. In this case, hot gases are allowed to escape through a vessel that is packed with a refractory material until the packing is hot. Air or other cool gas is then fed back to the plant through the hot bed, thereby pre-heating the air or gas feed.

Another factor, in addition to the packing shape and surface area, is the liquid and vapor distribution that enters the packed bed. The number of theoretical stages required to make a given separation is calculated using a specific vapor-to-liquid ratio. If the liquid and vapor are not evenly distributed across the superficial tower area as it enters the packed bed, the liquid-to-vapor ratio will not be correct and the required separation will not be achieved. The packing will appear to not be working in the correct manner. Also, the packed bed columns can contain liquid distributors and redistributors which help to distribute the liquid evenly over a section of packing, increasing the efficiency of the mass transfer.^[1] The design of the liquid distributors used to introduce the feed and reflux to a packed bed is critical to making the packing perform at maximum efficiency.

See also: Packed Bed Reactor, Packed Scrubber.

Packed Bed Reactor

A packed bed reactor (also known as a fixed bed reactor) is the most commonly applied reactor in the crude oil and energy industries. In the reactor, the catalyst particles (usually in the form of pellets with the particle diameter varying from a several millimeters to several centimeters) are placed in a tube, through which the fluid is passed. Generally, the catalyst particles are immobile. Excessively small particle sizes are avoided since they start moving as the flow velocity increases. Additionally, small particles cause a drop in the pressure in the reactor. On the other hand, when using large catalyst particles, the diffusion distance to the active sites inside the catalyst increases.

In the simplest form, a catalytic reactor consists of a cylindrical tube packed with small catalyst pellets and ‘surrounded’, in the case of an exothermic reaction, by a cooling medium. Reactant gases enter the bottom of the reactor, and the reaction occurs on the surface of the catalyst. Because of the presence of the cooling medium, the temperature at the center of the reactor will be higher than that at the tube wall. As a result, the reaction rate will be much higher at the center than at the wall and accordingly, the products of the reaction will tend to accumulate at the center while the reactants are accumulating at the wall.

The design of a packed bed is influenced by the structure of the packing matrix, which in turn is governed by the shape, dimensions, and the loading of the constituent particles. For reactor applications, the optimum design of catalyst pellet in terms of shape configuration, internal pores, and available surface area can promote catalytic activity and the prevailing transport properties of the system. Also, at the design stage, resistance to crushing and abrasion, as well as dust build-up, should also be taken into account. Knowledge of the underlying factors should enable designers to design the optimum configuration for a given system with prescribed conditions.

The bed of catalyst pellets is generally considered as if it is a continuous homogeneous media, and the physical properties of the packed bed or system are assigned values on the basis of a weighted average of each of the individual constituents making up the system. The weighting procedure is, in almost all cases, determined by a macroscopic or

bulk contribution of all the components present in the system. The properties, such as (i) porosity, (ii) mass velocity, and (iii) thermal conductivity will vary smoothly throughout the packed bed and, as a consequence, the solution of the differential equations representing the heat, mass, and momentum distributions will necessarily give rise to, correspondingly, smoothly varying values of temperature, concentration, and velocity.

See also: Fixed Bed Reactor or Moving Bed Reaction, Packed Bed, Packed Bed Scrubber.

Packed-Bed Scrubber

A packed-bed scrubber consists of a bed of packing elements, such as coke, broken rock, rings, saddles, or other manufactured elements. The packing breaks down the liquid flow into a high-surface-area film so that the dusty gas streams passing through the bed achieve maximum contact with the liquid film and become deposited on the surfaces of the packing elements. This type of scrubber has a high collection efficiency for respirable dust.

The packed bed scrubber, or packed tower, is designed to remove gaseous or vaporous pollutants from an air stream. The process is accomplished by contacting the contaminated air stream with scrubbing liquor that absorbs or chemically reacts with the pollutants. Some vapors can be simply removed by condensation through the cooling effect of the circulating liquid. The cleaned air is then discharged to the atmosphere, and the contaminated scrubbing liquor is either disposed of in an approved manner or chemically treated and recycled. In some cases, the collected contaminants can be recovered and reused in the original or other processes.

In order to optimize the contaminant removal efficiency, the contact between the contaminated air and the scrubbing liquor must be maximized. To achieve this, specially designed packing materials are used to fill the tower to a specified depth. The combination of packing material, packing design, depth of packing, bed velocity, and the scrubbing liquor chemistry and amount all combine to achieve the desired results. Since every system must be looked at individually, each unit is custom tailored to meet the specific needs of the application. Therefore, system size is virtually unlimited and scrubbers of all sizes are in use.

This countercurrent vertical scrubber is most commonly used for the removal of noxious gases from gas streams. It is designed for high collection efficiencies and maximum corrosion resistance.

See also: Packed Bed, Packed Bed Reactor.

Paraffin Hydrocarbons

The proportion of paraffins in crude oil varies with the type of crude, but within any one crude oil, the proportion of paraffinic hydrocarbon derivatives usually decreases with increasing molecular weight and there is a concomitant increase in aromaticity and the relative proportion of heteroatoms (nitrogen, oxygen, and sulfur).

The relationship between the various hydrocarbon constituents of crude oils is one of hydrogen addition or hydrogen loss. This is an extremely important aspect of crude oil composition, and there is no reason to deny the occurrence of these inter-conversion schemes during the formation, maturation, and *in situ* alteration of crude oil. Indeed, a scheme of this type lends even more credence to the complexity of crude oil within the hydrocarbon series alone and also supports current contentions that the high-molecular-weight constituents (resin constituents and asphaltene constituents) are structurally related to the lower-boiling constituents rather than proposals that invoke the existence of highly condensed polynuclear aromatic systems.

The abundance of the different members of the same homologous series varies considerably in absolute and relative values. However, in any particular crude oil or crude oil fraction, there may be a small number of constituents forming the greater part of the fraction, and these have been referred to as the *predominant constituents*. This generality may also apply to other constituents and is very dependent upon the nature of the source material as well as the relative amounts of the individual source materials prevailing during maturation conditions.

Normal paraffin hydrocarbon derivatives (*n*-paraffins, straight-chain paraffins) occur in varying proportions in most crude oils. In fact, paraffinic crude oil may contain up to 20 to 50% w/w *n*-paraffins in the gas oil fraction. However, naphthenic or asphaltic crude oils sometimes contain only small amounts of normal paraffins.

Considerable quantities of *iso-paraffins* have been noted to be present in the straight-run gasoline fraction of crude oil. The 2- and 3-methyl derivatives are the most abundant, and the 4-methyl derivative is present in small amounts. If at all, it is generally accepted that the slightly branched paraffins predominate over the highly branched materials. It seems that the *iso*-paraffins occur throughout the boiling range of crude oil fractions. The proportion tends to decrease with increasing boiling point; it appears that if the *iso*-paraffins are present in lubricating oils, their amount is too small to have any significant influence on the physical properties of the lubricating oils.

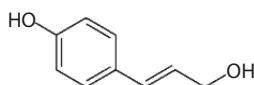
As the molecular weight (or boiling point) of the crude oil fraction increases, there is a concomitant decrease in the amount of free paraffins in the fraction. In certain types of crude oil, there may be no paraffins at all in the vacuum gas oil fraction. For example, in the paraffinic crude oils, free paraffins will separate as a part of the asphaltene fraction but in the naphthenic crude oils, free paraffins are not expected in the gas oil and asphaltene fractions.

The vestiges of paraffins in the higher-molecular-weight fractions typically occur as alkyl side chains on aromatic and naphthenic systems, and these alkyl chains can contain forty or more carbon atoms.

See also: Alkanes.

Paracoumaryl Alcohol

Paracoumaryl alcohol (*p*-coumaryl alcohol) is a phytochemical one of the monolignols. It is a white solid and is a major precursor to lignin or lignans.



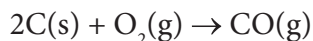
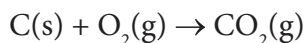
Paracoumaryl alcohol (*p*-coumaryl alcohol)

See also: Coniferyl Alcohol, Lignin, Sinapyl Alcohol.

Partial Oxidation

Partial oxidation (often referred to as POX or P_{ox}) is the reaction that occurs when a less-than full stoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich synthesis gas (syngas), which can then be put to further use, for example in the production of hydrocarbon fuels or oxygenates. In fact, the majority of gasifiers are partial oxidation reactors, in which just sufficient air or oxygen is introduced to burn part of the input biomass to provide the heat for pyrolysis and gasification.

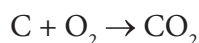
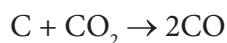
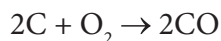
For example, the combustion of a carbonaceous feedstock such as coal involves reaction with oxygen, which may be supplied as pure oxygen or as air, and forms carbon monoxide and carbon dioxide. Principal chemical reactions between carbon and oxygen involve:



If sufficient air or oxygen is supplied, combustion proceeds sequentially through vapor-phase oxidation and ignition of volatile matter to eventual ignition of the residual char. Certainly, it is not desirable to carry out the combustion reaction too much since it represents a wasteful use of carbonaceous resources.

Even though the combustion or oxidation reactions of carbon may be expressed in terms of simple stoichiometric reaction equations, partial oxidation involves a complex reaction mechanism that depends on how fast and

efficiently combustion progresses. The reaction pathway is further complicated due to the presence of both gas-phase homogeneous reactions and heterogeneous reactions between gaseous and solid reactants. The early controversy involving the carbon oxidation reaction centered on whether carbon dioxide is a primary product of the heterogeneous reaction of carbon with oxygen or a secondary product resulting from the gas-phase oxidation of carbon monoxide. Oxidation of carbon involves at least the following four carbon-oxygen interactions of which only two are stoichiometrically independent:



It is generally agreed concerning the carbon-oxygen reaction that (i) carbon dioxide, as well as carbon monoxide, is a primary product of carbon oxidation, (ii) the ratio of the primary products, carbon monoxide to carbon dioxide, is generally found to increase sharply with increasing temperature, and (iii) there is lack of general agreement in that the magnitude of the ratio of the primary products is a sole function of temperature and independent of the carbon reacted.

A distinction is made between thermal partial oxidation (TPOX) and catalytic partial oxidation (CPOX). For example, thermal partial oxidation reactions, which are dependent on the air-fuel ratio, proceed at temperatures in excess of 1,200°C (2,190°F). In catalytic partial oxidation, the use of a catalyst reduces the required temperature to approximately 800 to 900°C (1,470 to 1,650°F).

The choice of method depends on the sulfur content of the fuel being used – catalysts can be employed if the sulfur content is below 50 ppm – higher sulfur content would poison the catalyst, and the thermal method is preferable for such fuels.

See also: Carbonization, Gasification, Gasification of Biomass.

Particulate Matter

Particulate matter (particulates, fine particles) are tiny particles of solid or liquid suspended in a gas. Some particulates occur naturally, originating from volcanoes, dust storms, forest and grassland fires, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants, and various industrial processes also generate significant amounts of aerosols. Averaged over the globe, anthropogenic aerosols – those made by human activities – currently account for approximately 10% of the total amount of aerosols in the atmosphere. Increased levels of fine particles in the air are linked to health hazards.

The detrimental environmental effects of particulate matter on the atmosphere have been of some concern for several decades. The total output of particulate matter into the atmosphere has increased in Europe since medieval times and, although the sources are various, there is special concern because of the issue of particulate matter from fossil fuel use. Species such as mercury, selenium, and vanadium which can be ejected into the atmosphere as a result of fossil fuel combustion are particularly harmful to the flora and fauna. There is the need to remove such materials from gas streams that are generated during fossil fuel processing and use.

The most common categorizations imposed on particulates are those with respect to size. The most widely used definition is the aerodynamic diameter. The notation PM10 is used to describe particles of 10 micrometers or less, and PM2.5 represents particles less than 2.5 micrometers in aerodynamic diameter. However, all reference methods allow a high margin of error which is referred to with other equivalent numeric values (Table P-1).

Table P-1 Size ranges for particulate matter.

Fraction designation	Size Range microns (μm)
PM ₁₀	Less than or equal to 10
PM _{2.5}	Less than or equal to 10
PM ₁	Less than or equal to 10
Ultrafine (UFP or UP)	Less than or equal to 10
PM ₁₀ -PM _{2.5} (coarse fraction)	2.5 μm to 10

In some specialized settings, each fraction may exclude the fractions of lesser scale, so that PM₁₀ excludes particles in a smaller size range, e.g., PM_{2.5}, usually reported separately. Such a case is sometimes emphasized with the difference notation, e.g., PM₁₀-PM_{2.5}.

Particulate matter consists of the minute separate airborne particles that are emitted from oil shale operations. Particulate matter is one of the criteria pollutants under the Clean Air Act.

See also: Gas Cleaning, Gas Processing, Gas Treating, Particulate Matter Control, Particulate Matter Removal.

Particulate Matter Control

Particulate matter control (often referred to as dust control) has been one of the primary concerns of industries, since the emission of particulate matter is readily observed through the deposition of fly ash and soot as well as in impairment of visibility. Differing ranges of control can be achieved by use of various types of equipment. Upon proper characterization of the particulate matter emitted by a specific process, the appropriate piece of equipment can be selected, sized, installed, and performance tested.

Particulate matter (PM) control technologies include electrostatic precipitators (ESPs), fabric filters (FFs) (also called “baghouses”), and particulate scrubbers (PS). Electrostatic precipitators and fabric filters may be classified as either cold-side (CS) devices – installed upstream of the air heater where flue gas temperatures range from 140 to 160°C (285 to 320°F) – or hot-side – installed downstream of the air heater and operate at temperatures ranging from 350 to 450°C (650 to 840°F).

See also: Gas Cleaning, Gas Processing, Gas Treating, Particulate Matter, Particulate Matter Removal.

Particulate Matter Removal

There are many types of particulate collection devices in use, and they involve a number of different principles for removal of particles from gas streams. Selection of an appropriate particle removal device must be based upon equipment performance as anticipated/predicted under the process. Such equipment includes cyclone collectors, electrostatic precipitators, and wet scrubbers.

Cyclones collectors utilize the principle of centrifugal force to separate particulates from a gas stream. Vortex flow is induced by the design of the gas inlet duct, and the main vortex is characterized by axial flow away from the gas inlet and radial flow outward from the ads of the cyclone body. The central core has the same rotary direction, but the axial and radial velocity components are in the opposite direction to that of the main vortex. The major requirements of the dust discharge are that upward gas flow into the cyclone body should be minimal, while continuous discharge of the dust is maintained. This is often accomplished by the inclusion of baffles or straightening vanes at the discharge to suppress the vortex at this point, thus minimizing up-flow.

Cyclones have many potential applications in coal gasification systems. Efficiency can be low for collecting particles smaller than 10 microns, but above this size, collection efficiency can be at least 90%. Conventional applications for cyclones include use as precleaners, entrainment separators, and for controlling dust emissions from coal grinding and pulverizing.

Electrostatic precipitators are efficient collectors of fine particulate matter and are capable of reducing the amount of submicron particles by 90%, or more. They have the capability of collecting liquid mists as well as dust. The basic components of a precipitator are the discharge (or corona) electrode, the collection electrode (plates), and the precipitator shell. Other components are the dust hopper, high-voltage equipment, and gas distributors. Suspended particles are charged by collisions with the negative ions passing through the zone between the corona and the collection electrode. Movement of the particles to the collection electrode is governed by the interaction of the electric field and charged particles in the moving gas stream.

Granular-bed filters use a bed of separate, packed granules which serve as the filter medium and have the ability to collect particulates from gas streams not only at low-temperatures but also (depending on bed structure) at high temperature and pressure. These filters (again depending on bed characteristics) can be used for simultaneous control of particulates and hydrogen sulfide (by adsorption) high temperature.

Granular bed filters are classified according to the method used to remove collected dust from the filter medium, thus: (i) continuously moving, (ii) intermittently moving, or (iii) fixed-bed filters. Cleaning is required to prevent interstitial plugging, which can cause pressure drop. This requirement distinguishes granular bed filters from fluidized-bed systems, which utilize the product gas to keep the granules in motion and prevent plugging.

Continuously moving systems may be arranged in a cross-flow configuration in which the gas passes horizontally through the granular layer, while the granules and collected dust move continuously downward and are collected at the bottom. The dust and granules are then separated and the cleaned granules returned to the bed. In the intermittently moving-bed concept, the bed is stationary during filtration. Accumulated dust and the surface layer of granules are removed from the panel by a backwash pulse and replaced by fresh granules from the overhead hoppers. Fixed-bed systems use either backwash air and/or mechanical agitation to remove collected dust.

Wet scrubbers are used when hot raw gas is to be cooled directly or if it has already been cooled in a waste-heat recovery system. Wet scrubbers are devices that utilize gas/liquid contacting to cool the gas stream, condense high-boiling hydrocarbon derivatives, dissolve some constituents, and separate particles from gas streams. There are many different wet scrubber designs, and a type that has been widely applied to coal gas is the venturi scrubber. Gas streams are passed through a tube to contact with water, which is added at the throat. The throat promotes intimate mixing of the gas and liquid. The liquid, which forms droplets ranging in size from 100 to 1,000 microns, collects particulates mainly by inertial impaction.

Other wet scrubber designs that can be applied to coal gas are plate scrubbers (sieves, bubble caps, and impingement plates), massive packing (rings, saddles), fibrous packing (plastic, spun glass, fiber glass, and steel wool), centrifugal (cyclone), and directional baffles (louvres, zigzags, disk, and donut).

See also: Gas Cleaning, Gas Processing, Gas Treating, Particulate Matter, Particulate Matter Control.

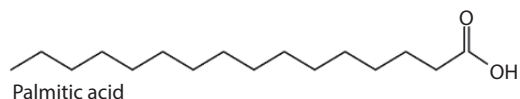
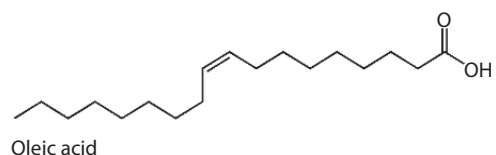
Peanut Oil

Peanut oil, also known as groundnut oil or arachis oil, is a vegetable oil-derived from peanuts. There are several varieties of peanut oil on the market today. From refined, 100% peanut oil to blends of oil.

Refined peanut oil is the most common form of peanut oil used for cooking. This oil has been refined to remove flavors and colors, making it a neutral oil. Virgin or cold-pressed peanut oil is oil that has not been refined and retains much of the properties. Roasted peanut oil is the oil-derived peanuts that have been roasted prior to expelling the oil, which provides a deep nutty flavor and dark golden brown color. Peanut oil blends are the results of blending peanut oil with other natural oils, such as soybean oil.

The various varieties of peanuts may be the future of peanut biodiesel because it can be planted and grown with just one herbicide application for weed control, compared to the three to four applications typically sprayed during a growing season for edible peanuts. Additionally, these fuel peanuts are grown without fungicides, which are the greatest input cost in traditional peanut production. Promising varieties also include DP-1 and Georgia-04S, a new high-oleic-acid, Spanish-type peanut. Production of these peanuts would be limited to the southern regions of the United States where growing conditions are more suitable.

Peanut oil, also known as groundnut oil or arachis oil, is composed of fatty acids such as oleic acid, palmitic acid, and other fatty acids.



Peanut oil could be used as a source of fuel for the diesel engine and was one of the earliest demonstrations of biodiesel technology.

See also: Biodiesel.

Peat

Peat, while being generally assigned as a precursor to coal (in fact, it is the bottom rung of the coal origin and maturation ladder) is also considered as a plentiful supply (when treated in the appropriate manner) of alternate fuels and an alternate source of energy.

Peat is partially matured plant matter, formed by slow decay in water such as found in locations variously called bogs, moors, muskegs, pocosins, mires, and peat swamps. Peat forms when plant material, usually in marshy areas, is inhibited from decaying fully by acidic and anaerobic conditions. It is composed mainly of marshland vegetation: trees, grasses, fungi, as well as other types of organic remains, such as insects, and animal corpses, which may be of some value to archaeologists.

Peat layer growth and the degree of decomposition (or humification) depends principally on its composition and on the degree of waterlogging. Peat formed in very wet conditions accumulates considerably faster, and is less decomposed, than that in drier places. This allows climatologists to use peat as an indicator of climatic change. The composition of peat can also be used to reconstruct ancient ecologies by examining the types and quantities of its organic constituents.

Peat material is fibric, hemic, or sapric. Fibric peat is the least decomposed, and comprise intact fiber. Hemic peat is somewhat decomposed, and sapric peat is the most decomposed. Phragmites peat is composed of reed grass (*Phragmites australis*) and other grasses and is denser than many other types of peat.

Peat is soft and easily compressed when water in the peat is forced out. When dried, peat can be used as a fuel and has industrial importance as a fuel in some countries, such as Ireland and Finland, where it is harvested on an industrial scale. Although peat has many uses, it also presents severe problems at times. When dry, it can be a major fire hazard, as peat fires can burn almost indefinitely (or at least until the fuel is exhausted), even underground, provided there is a source of oxygen. Peat deposits also pose major difficulties to builders of structures, roads, and railways, as they are highly compressible under even small loads.

See also: Peat Swamp and Peat Swamp Forest.

Peat Swamp and Peat Swamp Forest

The term peat swamp (in reality, a complex chemical and environmental entity) is used to mean the initial products of the anaerobic decay of the fallen trees (woody material). It is not, however, meant to show any compliance with the consecutive theory in which peat is gradually converted (metamorphosed) to coal by a series of sequential chemical and physical transformations. The converse is also true insofar as use of convenient, perhaps archaic, terminology does not mean rejection of a theory which advocates the concepts of concurrent chemical transformation without the insertion of coal-types as intermediate products in the sequence.

Peat swamp forests are tropical moist forests where waterlogged soil prevents dead leaves and wood from fully decomposing. Over time, this creates a thick layer of acidic peat. Large areas of these forests are being logged at high

rates. Peat swamp forests are typically surrounded by lowland rain forests on better-drained soils, and by brackish or salt-water mangrove forests near the coast.

Tropical peatlands, which coexist with swamp forests within the tropical and subtropical moist broadleaf forests biome, store and accumulate vast amounts of carbon as soil organic matter. In fact, tropical peatlands has important implications for climate change; they are among the largest near-surface reserves of terrestrial organic carbon. Peat swamp forests, which have ecological importance, are one of the most threatened, yet least studied and most poorly understood biotypes.

Tropical peat swamp forests are home to thousands of animals and plants, including many rare and critically endangered species such as the orangutan and Sumatran tiger, whose habitats are threatened by peatland deforestation.

See also: Peat.

Pelletization

Pelletization (pelletizing) is the formation of pellet-like products from solid carbonaceous materials such as char and coke. The materials used for pelletizing fuels generally have a size consistency below 0.004 inch, and the majority of the particles are smaller than 0.002 inch. Addition of liquid on rotating disks or drums agglomerates the fuel to spherical shapes. The strength of the pellets depends on the water content of the agglomerated material and is greatest when the optimum action of the capillary forces of the water is obtained.

A cold pelletizing process for the carbonization of char or coke pellets involves heating the pellets at heated to 550 to 650°C (1,020 to 1,200°F) and subsequently carbonized with sand as heat carrier. In the second stage, the pellets are coated with hematite ore (Fe_2O_3) and the ore-covered pellets are then coked whereupon soften and sinter together to form a coherent coke. Addition of a high-boiling oil to the char/coke increases the stability of the pellets in the oven.

A hot pelletizing process shapes the pellet in the chosen temperature range, possibly in the presence of binder, using pelletizing equipment. An advantage is the possibility of mixing in larger amounts of binder than can be done in briquetting. The binder cokes at the temperatures that are used during pellet shaping, and the possibility of desulfurizing the coke pellets during calcining is possible by addition of hydrogen under pressure.

Pellets and Briquettes

Pellets are a fuel in the form of short cylindrical or spherical units. It is usually 6-12 mm in diameter and 10-30 mm in length, with a moisture content of less than 10%.

Pellets are generally produced from residues of wood processing industries and mainly used for heating and electricity production purposes. Pellets are especially suitable in small heating systems due to their automatic heating process, easy storage as they do not degrade, relatively low cost, and a low yield of ash.

From the three most commonly used types of wood (logs, wood chips, and wood pellets), pellets offer major advantages for small heating systems and together with wood chips (which, contrary to pellets, are best suited for a large-scale use) are a best renewable fuel alternative to fossil fuels in the future. This type of bioenergy is efficient, clean, and reliable. In comparison with other solid biofuels, pellets provide the following advantages and disadvantages:

Pellets are generally manufactured from sawdust – a by-product of sawmilling, shavings, grinding dust, bark, and finely reduced wood waste, some of which comes from further processing of wood chips.

The demand for pellets is increasing, and other biomass wastes will be considered as raw materials. Therefore, logging residues, energy crops, and its residues (ex. straw), agricultural waste, and other organic fractions of household waste could be used for pellet production.

However, these new fuels might release a higher amount of emissions due to incomplete combustion, so their use must be studied carefully before introduction to the residential market.

In general, wood pellets can be produced from 4 main types of biomass: woody biomass, herbaceous biomass, fruit biomass, and peat.

Pellets made of compressed sawdust or wood shavings have been available in many parts of the world for more than several decades. Because they are compressed, pellets offer a more concentrated form of fuel than wood chips. Consequently, they need less storage space and are easier to handle. The manufacture of wood pellets requires more energy than woodchips, and the capital cost for production plant is high; pellets are therefore more expensive than chips.

Pellets can be used to fuel a variety of appliances and heating systems. The smallest are pellet stoves with outputs of up to around 9 kW which are suitable for heating individual rooms. These stoves are electronically controlled and can deliver regulated heat output and only need fueling once every few days. Pellet boilers are available in a wide range of outputs from small domestic scale to large industrial scale.

See also: Briquettes, Briquetting, Pelletization.

Percolation Filtration Process

The term percolation refers to the movement of fluids through porous materials, and filtration is the act or process of filtering which is the mechanical separation of the undissolved particles floating in a liquid. Thus, the percolation filtration process is a continuous-flow cyclic-regenerative liquid phase process in which oil is filtered through a bed (containing 10 to 50 tons of Fuller's earth – a clay mineral) before storage. Two or more beds are used alternately on an operating and regenerating cycle. The spent clay is regenerated by washing it with naphtha, steaming, and burning.

Activated Fuller's earth used in the percolation filter process is in the granular form; this process is usually used for light color oils like base oil distillates.

The percolation method is a simple process and consists of a vertical steel cylinder closed at both ends and provided with suitable man-heads and pipe connections at the top and bottom to permit the introduction and discharge of clay and oil. A perforated plate or a wire screen at a slight distance above the bottom is provided over which a heavy canvas blanket is placed and clamped to hold the clay in filter yet allow oil to pass through and out of the filter.

See also: Clay Minerals.

Perennial Systems for Biofuel Production

Several woody perennial plants can be grown for bio-fuels, while at the same time provide conservation benefits and ecological services that markedly exceed those associated with conventional annual crops like corn. In the United States, most research has focused willow shrubs (*Salix* spp.) and hybrid poplar (*Populus* spp.) production systems.

Hybrid poplars are predominantly cottonwoods and interspecific hybrids that have been selected and bred for fast growth. Sustained yields of 5 dry tons/acre/year have been documented in the north central United States and have reached 7 dry tons/acre/year on high productivity sites.

Another potentially large source of cellulose is agricultural residues (such as corn stalks), but the extent to which these can be sustainably removed from crop land each year without significantly lowering soil organic matter and overall soil quality is not fully appreciated.

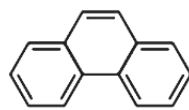
Timber belts are multiple row field windbreaks that are planted with commercially valuable, fast-growing trees (such as hybrid poplar or hybrid willow) to provide conservation benefits, improve adjacent crop yields, diversify on-farm income sources, and produce commercially valuable wood products. Various planting configurations have been developed that provide wind protection for soils and crops, and yield sufficient biomass to make wood harvest economical. Tree rows are oriented perpendicular to the prevailing wind to reduce wind velocity and improve the microclimate within the sheltered zone to enhance production of adjacent crops. Because of their rapid growth and range of marketable products, hybrid poplars fit well into the timber belt concept. The strategy is to harvest half of the rows in a timber belt at age 7 to 12, while the other half are left to provide continued wind protection. Within a few years, after the stumps have sprouted and re-established sufficient wind protection, the remaining rows are harvested. In this way, continuous wind protection and associated economic benefits to adjacent crops can be achieved.

Willow has several characteristics that make it ideal for woody crop systems, including high yields, ease of propagation, a broad genetic base, a short breeding cycle, and the ability to resprout after multiple harvests. A sustainable system has been devised for willow biomass production by planting unrooted stem cuttings at a density of 4,000-8,000 plants per acre. Willow can achieve high yields, typically reaching 15-25 feet in height in three years, at which time they can be harvested using modified agricultural equipment that cuts and chips the biomass in one operation. They resprout vigorously from their stumps (coppice) following harvest, with 7 to 8 harvesting cycles possible from an initial planting.

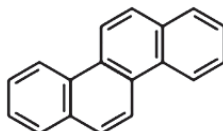
See also: Biomass, Wood.

Peri-Condensed Aromatic Compounds

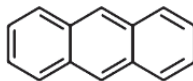
Peri-condensed aromatic compounds are based on angular condensed aromatic hydrocarbon systems, e.g., phenanthrene and chrysene are examples, and similar homologs, while anthracene and tetracene are examples of linear condensed aromatic hydrocarbon systems:



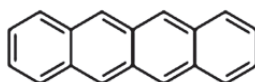
Phenanthrene



Chrysene



Anthracene



Tetracene

See also: Aromatic Hydrocarbons, Naphthalene and Polynuclear Aromatic Hydrocarbons, Polycyclic Aromatic Hydrocarbons, Polycyclic Compounds.

Periodic Table of the Elements

The Periodic Table of the Elements is an important reference item since it arranges all the known elements in an informative manner (Table P-2). The elements are arranged left to right and top to bottom in order of increasing atomic number, and the order generally coincides with increasing atomic mass. The different rows of elements are called periods, and the period number of an element signifies the highest energy level an electron in that element occupies (in the unexcited state). The number of elements in a period increases as one traverses down the periodic table because as the energy level of the atom increases, the number of energy sub-levels per energy level increases.

It is possible – using the data in the table – to extract information concerning individual elements. For instance, by examining the position of an element on the periodic table, it is possible to make an inference related to the electronic configuration of the element. Elements that lie in the same column on the periodic table (referred to as a

group) have identical valance electron configurations and consequently behave in a similar fashion chemically. The definitions related to the Periodic Table are as follows.

Atomic Number

The atomic number of an element, the number of protons in an atom, defines what element it is. For example, carbon atoms have six protons, hydrogen atoms have one, and oxygen atoms have eight. The number of protons in an atom is referred to as the atomic number of that element. The number of protons in an atom also determines the chemical behavior of the element.

Table P-2 The Periodic Table of the Elements.

1 H																		2 He
3 Li	4 Be																	
11 Na	12 Mg																	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 110	111 111	112 112		114 114		116 116		118 118	
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

Atomic Symbol

The atomic symbol is one or two letters chosen to represent an element (such as H for hydrogen), and these symbols are used internationally. Typically, a symbol is the truncated name of the element or the truncated Latin name of the element.

Atomic Mass

The atomic mass is the average mass of an element in atomic mass units (amu). Though individual atoms always have an integer number of atomic mass units, the atomic mass on the Periodic Table is stated as a decimal number because it is an average of the various isotopes of an element. Isotopes can have a weight either more or less than the average. The average number of neutrons for an element can be calculated by subtracting the number of protons (atomic number) from the atomic mass.

Electronic Configuration

The electronic configuration is the orbital description of the locations of the electrons in an unexcited atom. In fact, it can be predicted how an atom will react based upon the electron configuration, and properties such as stability, boiling point, and conductivity can be predicted. Typically, only the outermost electron shells matter in reaction chemistry, so the inner electron shell notation can be truncated by replacing the long-hand orbital description with the symbol for a noble gas in brackets. This method of notation vastly simplifies the description for large molecules.

See also: Heavy Metals.

Permeability

Permeability (the unit of permeability is the Darcy) is the property of solids (such as rocks and in some cases, catalysts) that is an indication of the ability for fluids (gas or liquid) to flow through the solid. High permeability will

allow fluids to move rapidly through solid. For example, sandstones may vary in permeability from less than one to over 50,000 millidarcies (md). Permeabilities are more commonly in the range of tens to hundreds of millidarcies. A solid with 25% porosity and a permeability of 1 md will not yield a significant flow of water.

The effective permeability: a relative measure of the conductivity of a porous medium for a fluid when the medium is saturated with more than one fluid. A fundamental principle is that the total of the effective permeability is less than or equal to the absolute permeability which is the ability of a solid to conduct a fluid when only one fluid is present in the pores of the rock.

See also: Porosity.

Petrochemicals

The chemical industry is in fact the chemical process industry by which a variety of chemicals are manufactured. The chemical process industry is, in fact, sub-divided into other categories that are (i) chemicals and allied products in which chemicals are manufactured from a variety of feedstocks and may then be put to further use, (ii) rubber and miscellaneous products which focuses on the manufacture of rubber and plastic materials, and (iii) crude oil refining and related industries. The petrochemical industry falls under the sub-category of crude oil and related industries.

The term petrochemicals is often applied to individual chemicals produced from crude oil (Table P-3, Table P-4) which are then used as precursors to a wide range of other products such as polymers and plastics. Also, natural product chemicals as might constitute the various type of biomass could conceivably be the starting point for a biomass-based petrochemicals industry. In fact, biomass gasification leading to product gases suitable for the production of chemicals by the Fischer-Tropsch process is well documented.

Table P-3 Production of petrochemicals during refining.

Starting material	Process	Product
Petroleum	Distillation	Light ends
		methane
		ethane
		propane
		butane
	Catalytic cracking	ethylene
		propylene
		butylenes
		higher olefins
		ethylene
coking	propylene	
	butylenes	
	higher olefins	
Natural gas	refining	methane
		ethane
		propane
		butane

However, the definition of petrochemicals has been broadened to include the whole range of organic chemicals including chemicals from renewable energy sources. In many instances, a specific chemical included among the petrochemicals may also be obtained from other sources, such as coal, coke, or vegetable products. For example, materials such as benzene and naphthalene can be made from either crude oil or coal, while ethyl alcohol may be of petrochemical or vegetable origin. This makes it difficult to categorize a specific substance as, strictly speaking, petrochemical or non-petrochemical.

Table P-4 Properties of selected petrochemicals.

	Molecular weight	Specific gravity	Boiling point	Ignition temperature	Flash point	Flammability limits in air
			degrees F	degrees F	degrees F	% v/v
Benzene	78.1	0.879	176.2	1040	12	1.35-6.65
n-Butane	58.1	0.601	31.1	761	-76	1.86-8.41
iso-Butane	58.1		10.9	864	-117	1.80-8.44
n-Butene	56.1	0.595	21.2	829	Gas	1.98-9.65
iso-Butene	56.1		19.6	869	Gas	1.8-9.0
Ethane	30.1	0.572	-127.5	959	Gas	3.0-12.5
Ethylene	28.0		-154.7	914	Gas	2.8-28.6
n-Hexane	86.2	0.659	155.7	437	-7	1.25-7.0
n-Heptane	100.2	0.668	419.0	419	25	1.00-6.00
Methane	16.0	0.553	-258.7	900-1170	Gas	5.0-15.0
Naphthalene	128.2		424.4	959	174	0.90-5.90
Neohexane	86.2	0.649	121.5	797	-54	1.19-7.58
Neopentane	72.1		49.1	841	Gas	1.38-7.11
n-Octane	114.2	0.707	258.3	428	56	0.95-3.2
iso-Octane	114.2	0.702	243.9	837	10	0.79-5.94
n-Pentane	72.1	0.626	97.0	500	-40	1.40-7.80
iso-Pentane	72.1	0.621	82.2	788	-60	1.31-9.16
n-Pentene	70.1	0.641	86.0	569	-	1.65-7.70
Propane	44.1		-43.8	842	Gas	2.1-10.1
Propylene	42.1		-53.9	856	Gas	2.00-11.1
Toluene	92.1	0.867	321.1	992	40	1.27-6.75
Xylene	106.2	0.861	281.1	867	63	1.00-6.00

Petrochemicals are chemicals derived from natural gas and crude oil and, for convenience of identification, petrochemicals can be divided into two groups: (i) primary petrochemicals and (ii) intermediates and derivatives. Primary petrochemicals include olefin derivatives (ethylene, propylene, and butadiene), aromatic derivatives (benzene, toluene, and xylenes), and methanol. Petrochemical intermediates are generally produced by chemical conversion of primary petrochemicals to form more complicated derivative products. Petrochemical derivative products can be made in a variety of ways: directly from primary petrochemicals; through intermediate products which still

contain only carbon and hydrogen; and, through intermediates which incorporate chlorine, nitrogen, or oxygen in the finished derivative. In some cases, they are finished products; in others, more steps are needed to arrive at the desired composition.

In addition, there are four general types of petrochemicals: (i) aliphatic compounds, (ii) aromatic compounds, (iii) inorganic compounds, and (iv) synthesis gas (carbon monoxide and hydrogen). Synthesis gas is used to make ammonia (NH_3) and methanol (methyl alcohol, CH_3OH). Ammonia is used primarily to form ammonium nitrate (NH_4NO_3), a source of fertilizer. Much of the methanol produced is used in making formaldehyde ($\text{HCH}=\text{O}$). The rest is used to make polyester fibers, plastics, and silicone rubber.

An aliphatic petrochemical compound is an organic compound that has an open chain of carbon atoms, be it normal (straight), e.g., n-pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) or branched, e.g., iso-pentane [2-methylbutane, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$], or unsaturated. The unsaturated compounds, olefins, include important starting materials such as ethylene ($\text{CH}_2=\text{CH}_2$), propylene ($\text{CH}_3\text{CH}=\text{CH}_2$), butene-1 ($\text{CH}_3\text{CH}_2\text{CH}_2=\text{CH}_2$), iso-butene (2-methylpropene [$\text{CH}_3(\text{CH}_3)\text{C}=\text{CH}_2$]), and butadiene ($\text{CH}_2=\text{CHCH}=\text{CH}_2$).

Ethylene is the hydrocarbon feedstock used in greatest volume in the petrochemical industry. From ethylene, for example, are manufactured ethylene glycol, used in polyester fibers and resins and in antifreezes; ethyl alcohol, a solvent and chemical reagent; polyethylene, used in film and plastics; styrene, used in resins, synthetic rubber, plastics, and polyesters; and ethylene dichloride, for vinyl chloride, used in plastics and fibers. Propylene is also an important source of petrochemicals and is used in making such products as acrylics, rubbing alcohol, epoxy glue, and carpets. Butadiene is used in making synthetic rubber, carpet fibers, paper coatings, and plastic pipes.

An aromatic petrochemical is also an organic chemical compound but one that contains, or is derived from, the basic benzene ring system.

The petrochemical industry has grown with the crude oil industry and is considered by some to be a mature industry. However, as is the case with the latest trends in changing crude oil types, it must also evolve to meet changing technological needs. The manufacture of chemicals or chemical intermediates from a variety of raw materials is well established. And the use of natural gas and crude oil is an excellent example of the conversion of such raw materials to more valuable products. The individual chemicals made from natural gas and crude oil are numerous and include industrial chemicals, household chemicals, fertilizers, and paints, as well as intermediates for the manufacture of products, such as synthetic rubber and plastics.

Petrochemicals are generally considered chemical compounds derived from crude oil either by direct manufacture or indirect manufacture as by-products from the variety of processes that are used during the refining of crude oil. Gasoline, kerosene, fuel oil, lubricating oil, wax, asphalt, and the like are excluded from the definition of petrochemicals, since they are not, in the true sense, chemical compounds but are in fact intimate mixtures of hydrocarbon derivatives.

Petrochemicals are made, or recovered from, the entire range of crude oil fractions, but the bulk of petrochemical products are formed from the lower-boiling (C_1 to C_4) hydrocarbon gases as raw materials. These materials generally occur in natural gas, but they are also recovered from the gas streams produced during refinery, especially cracking, operations. Refinery gases are also particularly valuable because they contain substantial amounts of olefins that, because of the double bonds, are much more reactive than the saturated (paraffin) hydrocarbon derivatives. Also important as raw materials are the aromatic hydrocarbon derivatives (benzene, toluene, and xylene), that are obtained in rare cases from crude oil and, more likely, from the various product streams. By means of the catalytic reforming process, non-aromatic hydrocarbon derivatives can be converted to aromatics by dehydrogenation and cyclization.

The classification of materials as petrochemicals is used to indicate the source of the chemical compounds, but it should be remembered that many common petrochemicals can be made from other sources, and the terminology is therefore a matter of source identification.

The starting materials for the petrochemical industry are obtained from crude oil in one of two general ways. They may be present in the raw crude oil and, as such, are isolated by physical methods, such as distillation or solvent extraction. On the other hand, they may be present, if at all, in trace amounts and are synthesized during the refining operations. In fact, unsaturated (olefin) hydrocarbon derivatives, which are not usually present in crude oil, are nearly always manufactured as intermediates during the various refining sequences.

The manufacture of chemicals from crude oil is based on the ready response of the various compound types to basic chemical reactions, such as oxidation, halogenation, nitration, dehydrogenation addition, polymerization,

and alkylation. The low-molecular-weight paraffins and olefins, as found in natural gas and refinery gases, and the simple aromatic hydrocarbon derivatives have so far been of the most interest because it is individual species that can be readily be isolated and dealt with. A wide range of compounds is possible; many are being manufactured and progressing to the stage in which a sizable group of products is being prepared from the higher-boiling fractions of crude oil. For example, the various reactions of asphaltene constituents indicate that these materials may be regarded as containing chemical functions and are therefore different and are able to participate in numerous chemical or physical conversions to, perhaps, more useful materials. The overall effect of these modifications is the production of materials that either affords good-grade aromatic cokes comparatively easily or the formation of products bearing functional groups that may be employed as a non-fuel material.

For example, the sulfonated and sulfomethylated materials and their derivatives have satisfactorily undergone tests as drilling mud thinners, and the results are comparable to those obtained with commercial mud thinners. In addition, these compounds may also find use as emulsifiers for the *in situ* recovery of heavy (viscous) crude oil. These are also indications that these materials and other similar derivatives of the asphaltene constituents, especially those containing such functions as carboxylic or hydroxyl, readily exchange cations and could well compete with synthetic zeolites. Other uses of the hydroxyl derivatives and/or the chloro-asphaltene constituents include high-temperature packing or heat transfer media.

Reactions incorporating nitrogen and phosphorus into the asphaltene constituents are particularly significant at a time when the effects on the environment of many materials containing these elements are receiving considerable attention. Here, there is the potential that slow-release soil conditioners only release the nitrogen or phosphorus after considerable weathering or bacteriological action. One may proceed a step further and suggest that the carbonaceous residue remaining after release of the hetero-elements may be a benefit to humus-depleted soils, such as the gray-wooded and solonchic soils. It is also feasible that coating a conventional quick-release inorganic fertilizer with a water-soluble or water-dispersible derivative will provide a slower-release fertilizer and an organic humus-like residue. In fact, variations on this theme are multiple.

Nevertheless, the main objective in producing chemicals from crude oil is the formation of a variety of well-defined chemical compounds that are the basis of the petrochemical industry. It must be remembered, however, that ease of separation of a particular compound from crude oil does not guarantee its use as a petrochemical building block. Other parameters, particularly the economics of the reaction sequences, including the costs of the reactant equipment, must be taken into consideration.

See also: Biochemicals.

pH

The pH value is a means of expressing the acidity or alkalinity of a solution. At normal temperatures, *pure* water has a pH of 7 (neutral); the pH of a strong acid is approximately 1 and that of a strong base approximately 14.

The pH is the cologarithm of the activity of dissolved hydrogen ions (H^+). The hydrogen ion activity coefficients cannot be measured experimentally, so they are based on theoretical calculations. The pH scale is not an absolute scale; it is relative to a set of standard solutions whose pH is established by international agreement. To calculate the pH of an aqueous solution, it is necessary to know the concentration of the hydronium ion in moles per liter (molarity) from which the pH can be calculated using the expression:

$$pH = -\log [H_3O^+]$$

Also, the hydronium ion concentration can be calculated from the pH of the solution by the reverse of the mathematical operation employed to find the pH. Thus:

$$[H_3O^+] = 10^{-pH}$$

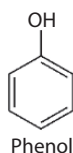
$$\text{or } [H_3O^+] = \text{antilog } (-pH)$$

pH is an important quantity that reflects the chemical conditions of a solution. The pH can control the availability of nutrients, biological functions, microbial activity, and the behavior of chemicals.

See also: Acidity and Alkalinity.

Phenol

Phenol (C_6H_5OH) is a key industrial chemical; however, the output of phenol from coal tar is exceeded by that of synthetic phenol.



Phenol has a low melting point (Table P-5); it crystallizes in colorless prisms and has a characteristic, slightly pungent odor. In the molten state, it is a clear, colorless, mobile liquid. At low temperature ($<68^{\circ}C$, $<154^{\circ}F$), the miscibility of phenol with water is limited, but above this temperature, the two are completely miscible.

Table P-5 Selected properties of phenol.

Chemical formula	C_6H_5O
Molar mass	$94.113 \text{ g}\cdot\text{mol}^{-1}$
Appearance	Transparent crystalline solid
Density	$1.07 \text{ g}/\text{cm}^3$
Melting point	$40.5^{\circ}C$ ($104.9^{\circ}F$; 313.6 K)
Boiling point	$181.7^{\circ}C$ ($359.1^{\circ}F$; 454.8 K)
Solubility in water	$8.3 \text{ g}/100 \text{ mL}$ ($20^{\circ}C$)
Vapor pressure	0.4 mmHg ($20^{\circ}C$) ^[3]

The melting and solidification points of phenol are quite substantially lowered by water. Phenol is readily soluble in most organic solvents (aromatic hydrocarbons, alcohols, ketones, ethers, acids, halogenated hydrocarbons, etc.) and somewhat less soluble in aliphatic hydrocarbons. Phenol forms azeotropic mixtures with water and other substances.

Phenol is used for the production of phenol-formaldehyde resins, while other important uses in the plastics field include the production of polyamides such as nylon, of epoxy resins and polycarbonates based on bisphenol A and of oil-soluble resins from p-t-butyl and p-octyl phenols. It is also used in the manufacture of pentachlorophenol which is used as a fungicide and in timber preservation. Aspirin and many other pharmaceuticals, certain detergents, and tanning agents are all derived from phenol, and another important use is in the manufacture of 2,4-dichlorophenoxyacetic acid (2,4-D) which is a selective weed-killer.

Phosphate Desulfurization

The phosphate desulfurization process uses potassium phosphate (K_3PO_4) as the active agent and is used in the same way as the Girbotol process to remove acid gases from liquid hydrocarbon derivatives as well as from gas streams. The treatment solution is a water solution of potassium phosphate (K_3PO_4), which is circulated through an absorber tower and a reactivator tower in much the same way as the ethanolamine is circulated in the Girbotol process; the solution is regenerated thermally.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Photolytic Oxidation Process

The photolytic oxidation process uses light to oxidize organic contaminants. They can be used in conjunction with chemical oxidizers. One technique that works well in many industrial situations is the combination of ultraviolet light and ozone gas. The process has the disadvantage of requiring relatively long residence times.

The photolytic oxidation process indirectly destroys volatile organic compounds (VOCs) in soil and groundwater. The process uses a xenon pulsed-plasma flash-lamp that emits short wavelength ultraviolet (UV) light at high intensity. The process strips the contaminants into the vapor phase, and the UV treatment converts the volatile organic compounds into less hazardous compounds.

Photolysis occurs when contaminants absorb sufficient UV light energy, transforming electrons to higher energy states and breaking molecular bonds. Hydroxyl radicals, however, are not formed. The process requires the UV light source to emit wavelengths in the regions absorbed by the contaminant.

The process uses vacuum extraction or air stripping to volatilize volatile organic compounds from soils or groundwater, respectively. Volatile organic compounds then enter the photolysis reactor, where a xenon flash lamp generates UV light. The plasma is produced by pulse discharge of electrical energy across two electrodes in the lamp. Ninety-nine percent destruction occurs within seconds, allowing continuous operation. Because organics are destroyed in the vapor phase, the process uses less energy than a system treating dissolved organics.

Photon

The photon is a type of elementary particle which is without mass and, hence, always moves at the speed of light in a vacuum. Photons are emitted in many natural processes. For example, when a charge is accelerated, it emits synchrotron radiation.

The photon is the quantum of the electromagnetic field including electromagnetic radiation such as light and radio waves, and the force carrier for the electromagnetic force. Photons are without mass (massless) and, thus, move at the speed of light in vacuum (approximately 186,282 miles per second). The photon belongs to the class of bosons. Like all elementary particles, photons are currently best explained by quantum mechanics and exhibit wave-particle duality, their behavior featuring properties of both waves and particles.

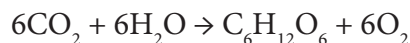
During a molecular, atomic, or nuclear transition to a lower energy level, photons of various energy will be emitted, ranging from radio waves to gamma rays. Photons can also be emitted when a particle and the corresponding antiparticle are annihilated as, for example, in the electron-positron annihilation.

See also: Boson, Electron, Nuclear Energy, Positron.

Photosynthesis

Photosynthesis is the principle agent for biomass production. In the process, light energy is used by chlorophyll-containing green plants to remove (or fix) carbon dioxide from the atmosphere and convert it to energy-rich organic compounds or biomass. Carbohydrate derivatives are usually the primary constituent of biomass, and cellulose is the single most important component. Starches are also important and predominate in storage organs such as tubers and rhizomes. Sugars reach high levels in fruits and in plants such as sugar cane and sugar beet. Lignin is a significant non-carbohydrate constituent of woody plant biomass.

Chemically, photosynthesis is the process by which chlorophyll-containing cells in green plants convert incident light to chemical energy, capturing carbon dioxide in the form of carbohydrates.



Photosynthesis takes place primarily in plant leaves, and little to none occurs in stems, etc. The parts of a typical leaf include the upper and lower epidermis, the mesophyll, the vascular bundle(s) (veins), and the stomates. The upper and lower epidermal cells do not have chloroplasts and, thus, photosynthesis does not occur there. They serve

primarily as protection for the rest of the leaf. The stomates are holes which occur primarily in the lower epidermis and are for air exchange: they let carbon dioxide in and oxygen out. The vascular bundles or veins in a leaf are part of the transportation systems of plants, moving water and nutrients around the plant as needed. The mesophyll cells have chloroplasts, and this is where photosynthesis occurs.

See also: Plants.

Photovoltaics

Photovoltaics (often abbreviated as PV) is the direct conversion of sunlight to electricity. Considered by many to be the most promising of the renewable electric technologies in the long term, it is an attractive alternative to conventional sources of electricity for many reasons: it is silent and non-polluting, requires no special training to operate, is modular and versatile, has no moving parts, and is reliable and largely maintenance-free. It can be installed almost anywhere, uses both direct and diffuse radiation, and can be incorporated into a variety of building products (roofing tiles and shingles, facades, overhangs, awnings, windows, atriums). Thus, the photovoltaic effect refers to the creation of an electrical current when light shines on a photosensitive material connected in an electrical circuit.

A photovoltaic cell (often called a solar cell) consists of layers of semiconductor materials with different electronic properties. In most of the current solar cells, the semiconductor is silicon, an abundant element in the crust of the Earth. By doping (i.e., chemically introducing impurity elements) most of the silicon with boron to give it a positive or p-type electrical character, and doping a thin layer on the front of the cell with phosphorus to give it a negative or n-type character, a transition region between the two types of doped silicon is formed that contains an electric field. This transition region is called a junction.

Light consists of energy packets called photons, and when light is incident on the cell, some of the photons are absorbed in the region of the junction and energy is transferred to the semiconductor, freeing electrons in the silicon. If the photons have enough energy, the electrons will be able to overcome the opposing electric field at the junction and move freely through the silicon and into an external circuit. These electrons stimulate current flow in the external circuit; the energy can be converted into work.

Photovoltaic systems for specific applications are produced by connecting individual modules in series and parallel to provide the desired voltage and current. Each module is constructed of individual solar cells also connected in series and parallel. Modules are typically available in ratings from a few peak watts to 250 peak watts.

Commercially available photovoltaic systems often include modules made from single-crystal or polycrystalline silicon or from thin layers of amorphous (non-crystalline) silicon. The thin-film modules use considerably less semiconductor material but have lower efficiencies for converting sunlight to direct-current electricity. Cells and modules are made from other thin-film photovoltaic materials.

Amorphous silicon modules experience a conversion efficiency loss of approximately 10% when initially exposed to sunlight, but then stabilize at the reduced figure. The mechanism for this reduction is being actively investigated, but is still not well understood. Individual modules made with other photovoltaic materials do not exhibit such loss of conversion efficiency, but combinations of modules in arrays do exhibit systematic reductions in power output over their lifetimes. Estimated at approximately 1% per year on average, based on data to date, these reductions are most likely associated with deteriorating electrical connections and non-module electrical components.

Complete photovoltaic systems require other components in addition to the photovoltaic modules. This "balance-of-system" generally includes a support structure for the modules to orient them properly to the sun, an inverter to convert direct-current electricity to alternating-current electricity, a storage system for electrical energy (usually batteries), an electronic charge regulator to prevent damage to the batteries by protecting against overcharging by the photovoltaic array and excessive discharge by the electrical load, and related wiring and safety features.

The output of a solar cell can be increased significantly by concentrating the incident sunlight onto a small area. Commercially available concentrator systems use low-cost lenses, mirrors, or troughs in conjunction with tracking systems to focus sunlight on a small, high efficiency but expensive solar cell. One-axis trackers follow the Sun during the day; two-axis trackers track daily and yearly variations in the Sun's position. The higher cost of the cell and the associated tracking equipment, and the inability to use diffuse radiation, are offset by the higher conversion efficiencies achieved.

The cost of photovoltaic electricity is largely determined by four factors: cost of the PV modules, the efficiency of converting sunlight to electricity, the balance-of-system costs, and the lifetime of the systems. There are many combinations of these factors that provide approximately the same cost of electricity. Modules are now available that are designed to last at least thirty years.

Another scheme that has been proposed for use of photovoltaics is the solar satellite power system. Such a system would place large individual PV arrays (up to ten megawatts peak power) in synchronous orbit around the earth, and beam the collected and converted solar energy through the atmosphere in the form of microwaves to large receiving antennas on Earth. The microwave generators would be powered by the photovoltaic electricity. The microwave energy collected at the surface would then be converted back to electricity for broad distribution.

See also: Photovoltaic Cells, Solar Power.

Photovoltaic Cells

Electricity can be produced from sunlight through a process called the photovoltaic (PV) effect. The term describes a process that produces direct electrical current from the radiant energy of the Sun. The photovoltaic effect can take place in solid, liquid, or gaseous material; however, it is in solids, especially semiconductor materials, that acceptable conversion efficiencies have been found. Solar cells are made from a variety of semiconductor materials and coated with special additives. The most widely used material for the various types of fabrication is crystalline silicon, representing over 90% of global commercial photovoltaic module production in its various forms.

A typical silicon photovoltaic cell (also called a solar cell), with a diameter of 4 in., can produce more than 1 W of direct current (DC) electrical power in full sun. Individual solar cells can be connected in series and parallel to obtain desired voltages and currents. These groups of cells are packaged into standard modules that protect the cells from the environment while providing useful voltages and currents. Photovoltaic modules are extremely reliable because they are solid state and have no moving parts. Silicon photovoltaic cells manufactured can provide over 40 years of useful service life.

Photovoltaic devices are made from semiconductor materials which are materials comprising those elements or compounds that have conductivity intermediate to that of metals or insulators. The three types of material structures commonly used to produce photovoltaics are (i) amorphous, with no order or periodicity within the compound, (ii) polycrystalline, with local order, visible grain boundaries, and bluish color; and (iii) single or monocrystalline, which is typified by long-range order and periodicity and is almost black with no visible grain boundaries. Furthermore, the crystalline structure of a semiconductor is important because when a small concentration of impurities (other elements such as phosphorus or boron) are introduced into the structure, the conductive properties of the material can radically change.

Cells for terrestrial applications are typically made from silicon as single-crystal, polycrystalline, or amorphous solids. Single-crystal silicon is the most efficient because the crystal is free of grain boundaries, which are defects in the crystal structure caused by variations in the lattice that tend to decrease the electrical and thermal conductivity of the material. They can be thought of as barriers to electron flow. Polycrystalline silicon has obvious grain boundaries. The portions of single crystals are visible to the naked eye. Amorphous silicon (a-Si) is the noncrystalline form of silicon where the atoms are arranged in a relatively haphazard way. Due to the disordered nature of the material, some atoms have a dangling bond that disrupts the flow of electrons. A dangling bond occurs when an atom is missing a neighbor to which it would be able to bind. Amorphous silicon has lowest power conversion efficiencies of the three types, but is the least expensive to produce.

Monocrystalline Silicon

The cells are made from an ingot of a single crystal of silicon, grown in high-tech labs, sliced, then doped and etched. For commercial terrestrial modules, efficiencies typically range from approximately 15 to 20%. Modules made of this type of cell are the most mature on the market. Reliable manufacturers of this type of photovoltaic module offer guarantees of up to 20–25 years at 80% of nameplate rating.

Polycrystalline Silicon

The cells are made up of various silicon crystals formed from an ingot. They are also sliced and then doped and etched. They demonstrate conversion efficiencies slightly lower than those of monocrystalline cells, generally from 13 to 15%. Reliable manufacturers typically guarantee polycrystalline photovoltaic modules for 20 years.

Amorphous Silicon

The term *amorphous* refers to the lack of any geometric cell structure. Amorphous modules do not have the ordered pattern characteristic of crystals as in the case of crystalline silicon. Commercial modules typically have conversion efficiencies from 5 to 10%. Most product guarantees are for 10 years, depending on the manufacturer.

Amorphous materials have found wide appeal for use in consumer devices (e.g., watches and calculators). It does have the advantage for some grid-tied or water-pumping systems in that higher voltage modules can be produced more cheaply than their crystalline counterparts. Another limiting factor to efficiency is that of traps in the material. Traps are semiconductor material impurities in the depletion region and can greatly increase recombination of electrons and holes.

A photovoltaic array is a group of modules that are electrically connected either in series or in parallel. The electrical characteristics of the array are analogous to those of individual modules, with the power, current, and voltage modified according to the number of modules connected in series or parallel. Maximum energy is obtained when the Sun's rays strike the receiving surface perpendicularly. In the case of photovoltaic arrays, perpendicularity between the rays of the Sun and the modules can be achieved only if the structural mounting of the modules allows the structure to follow the movements of the Sun.

Energy storage for photovoltaic systems commonly consists of batteries to store and discharge electrical energy as needed. However, each time a battery is charged or discharged, some energy is lost from the system. Batteries vary by type, depth of discharge, rate of charge, and lifetime (in photovoltaic applications). The most common types of batteries used with photovoltaic systems are lead-acid, but other more exotic and expensive batteries are sometimes used, such as nickel metal hydride. A new area of photovoltaic battery applications is emerging in which the photovoltaic battery is used for backup power when the utility grid fails for grid-tied photovoltaic systems. This application has unique battery charging and maintenance requirements. Batteries are usually installed in well-ventilated locations such as garages, utility rooms, and outbuildings to minimize the potential for capturing explosive concentrations of hydrogen gas and to minimize possible hazards from electrolyte spills.

Environmental Impact

While the widespread use of photovoltaic cells will reduce global warming by helping to cut down on the use of electricity created by the combustion of fossil fuels, the manufacture of this solar technology can be polluting. Most manufacturers use mercury to construct solar cells – mercury is a toxic waste that must be disposed of during the manufacture of the cells as well as after the cells have reached the end of their usefulness.

See also: Photovoltaics, Solar Energy.

Physical Solvent Processes

Physical solvent processes are processes that use a solvent to purify gas streams. Two of the currently most-widely-used physical solvent processes for gas cleaning are *Selexol* and *Rectisol* processes. The *Selexol* process solvent is the dimethyl ether of polyethylene glycol, while the *Rectisol* solvent is methanol.

The principal benefits of physical solvents are (i) high selectivity for hydrogen sulfide over carbonyl sulfide and carbon dioxide, (ii) high loadings at high acid gas partial pressures, (iii) stability of the solvent, and (iv) low heat requirements because most of the solvent can be regenerated by a simple pressure letdown.

The performance of a physical solvent can be easily predicted. The solubility of a compound in the solvent is directly proportional to its partial pressure in the gas phase, hence, the improvement in the performance of physical solvent processes with increasing gas pressure. Physical solvent processes can be easily configured to take advantage of their high hydrogen sulfide/carbon dioxide selectivity together with high levels of carbon dioxide recovery.

The Selexol process is a mixture of the dimethyl ethers of polyethylene glycol $[\text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3]$ where n is between 3 and 9. The solvent is chemically and thermally stable, and has a low vapor pressure that limits its losses to the treated gas. The solvent has a high solubility for carbon dioxide, hydrogen sulfide, and carbonyl sulfide. It also has appreciable selectivity for hydrogen sulfide over carbon dioxide.

The Selexol process can be configured in various ways, depending on the requirements for the level of hydrogen sulfide/carbon dioxide selectivity, the depth of sulfur removal, the need for bulk carbon dioxide removal, and whether the gas needs to be dehydrated. The gas stream from the low-pressure flash is combined with the acid gas from the regenerator. This combined gas stream is then sent to a sulfur recovery unit. However, the hydrogen sulfide content could be too low for use in a conventional Claus plant. However, the Selexol process can be configured to give a rich acid gas feed to the Claus unit as well as to provide for bulk carbon dioxide removal.

See also: Gas Cleaning, Claus Process, Selexol Process.

Physical Transformation Reactions

A physical conversion that is often ignored (or not recognized as such) is the change in composition that occurs when precipitation and dissolution reactions exert a major effect on the concentrations of inorganic ions in solution. Also included is the effect of adsorption and absorption on the composition of the pollutant.

The precipitation of a solid phase in environmental systems rarely results in a pure mineral phase. Minor elements such as cadmium can coprecipitate with major elements such as calcium to form a solid solution. In addition, the equilibrium activity of the component of a solid solution does not correspond to the solubility calculated from the solubility products of pure minerals. Furthermore, it is often impossible to distinguish chemically between a minor component coprecipitated in a solid, and the adsorption of that minor component onto the solids surface.

Also, complexation is an important process that will determine in some cases if mineral solubility limits are reached, the amount of adsorption that occurs, and the redox state that exists in the water. Inorganic chemicals can also form stable, soluble complexes with organic ligands. Ligands in leachates could include synthetic chelating agents (such as ethylenediamine), partially oxidized biodegradation products (such as organic acids), or natural humic materials. In fact, the movement of metals in the subsurface is strongly influenced by the concentration and chemical properties of ligands. However, the types and concentrations of ligands in most waste leachates is largely unknown.

Physical changes are changes affecting the form of an inorganic chemical but not always the chemical composition. Physical changes are used to separate mixtures into their component compounds, such as the use of liquid-solid chromatography, but cannot usually be used to separate compounds into chemical elements or simpler compounds. Thus, physical changes occur when objects or substances undergo a change that does not change their chemical composition. This contrasts with the concept of chemical change in which the composition of a substance changes or one or more chemicals combine or react (by combination or by degradation) to form new chemical products.

A common example that can be treated as a physical transformation is the settling of suspended sediment particles. Although settling does not actually transform the sediment into something else, it does remove sediment from the control volume by depositing it on the river bed. This process can be expressed mathematically by heterogeneous transformation equations at the river bed and can be considered to be a transformation process.

Another example of a physical change comes from the field of nuclear physics and is radioactive decay. Radioactive decay is the process by which an atomic nucleus emits particles or electromagnetic radiation to become either a different isotope of the same element or an atom of a different element. The three radioactive decay paths are alpha decay (the emission of a helium nucleus), beta decay (the emission of an electron or positron), and gamma decay (the emission of a photon). Gamma decay alone does not result in transformation, but it is generally accompanied by beta emission, which does.

More pertinent to the current text is the effect of sorption process and dilution on the properties of the contaminant.

Inorganic chemicals interact with the environment in different ways, and once a chemical is released into the environment, there are three physical effects that can influence the distribution of the chemicals: (i) absorption, (ii) adsorption, and (iii) dilution.

Physical Transformation Reactions – Absorption

Absorption is another phenomenon that can be a beneficial or adverse influence of the environment and involves the uptake of one chemical substance into the inner structure of another substance – most typically a gas into a liquid solvent. Furthermore, absorption is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase – gas, liquid, or solid material. This is a different process from *adsorption*, since molecules undergoing absorption are taken up by the volume, not by the surface (as in the case for adsorption). The process of absorption means that a substance captures and transforms energy and the absorbent distributes the material it captures throughout whole and adsorbent only distributes it through the surface.

In chemical absorption (sometimes referred to in the shortened word form as *chemisorption*), the absorbed material is generally converted to a product different to the starting material. Thus, chemical absorption or *reactive absorption* involves a chemical reaction between the absorbent (the absorbing substance) and the absorbate (the absorbed substance) and may be combined with the physical absorption phenomenon. This type of absorption depends upon the stoichiometry of the reaction and the concentration of the potential reactants.

Physical absorption or non-reactive absorption is made between two phases of matter: a liquid absorbs a gas, or a solid absorbs a liquid. When a liquid solvent absorbs a gas mixture or part of it, a mass of gas moves into the liquid. For example, water may absorb oxygen from the air. This mass transfer takes place at the interface between the liquid and the gas, at a rate depending on both the gas and the liquid. This type of absorption depends on the solubility of gases, the pressure, and the temperature. The rate and amount of absorption also depend on the surface area of the interface and its duration in time. For example, when the water is finely divided and mixed with air, as may happen in a waterfall or a strong ocean surf, the water absorbs more oxygen. When a solid absorbs a liquid mixture or part of it, a mass of liquid moves into the solid. This mass transfer takes place at the interface between the solid and the liquid, at a rate depending on both the solid and the liquid. Absorption is essentially a molecule attaching themselves to a substance and will not be attracted from other molecules.

On the other hand, chemical absorption or reactive absorption is a chemical reaction between the absorbed and the absorbing substances. Sometimes, it combines with physical absorption. This type of absorption depends upon the stoichiometry of the reaction and the concentration of its reactants.

See also: Absorption.

Physical Transformation Reactions – Adsorption

Adsorption is the physical accumulation of material (usually a gas or liquid) on the surface of a solid adsorbent and is a *surface phenomenon* (Calvet, 1989). Typically, adsorption processes remove solutes from liquids based on their mass transfer from liquids to porous solids. Ion exchange is the exchange of dissolved ions for ions on solid media. The process can be used to remove water hardness and toxic metals during wastewater treatment. Disinfection is the removal or inactivation of pathogenic organisms in wastewater prior to be discharged to the receiving body of water.

In nature, a variety of potential natural adsorbents exists in the soil – adsorption occurs in many natural, physical, biological, and chemical systems (especially in the environment) where inorganic molecules can adsorb on to minerals (such as clay) or on to charred wood that remains after a forest fire. In fact, clay minerals are particularly good adsorbents and have a high adsorption capacity for inorganic chemicals that have been released into the environment.

A natural clay mineral is not composed of one clay mineral only. Impurities such as calcite (CaCO_3), quartz (SiO_2), feldspar ($\text{KAlSi}_3\text{O}_8/\text{NaAlSi}_3\text{O}_8/\text{CaAl}_2\text{Si}_2\text{O}_8$), iron oxides, (FeO and Fe_2O_3) and humic acids (degradation products of organic materials) are the most common components in addition to the pure clay mineral. Calcite, iron oxides, and humic acids can be removed by chemical treatments. Quartz and feldspar can be removed by sedimentation if the particle size is bigger than that of the clay minerals, but traces of quartz are often found in the purified samples. Physically, clay minerals are typically ultrafine-grained [normally considered to be less than 2 micrometers (<2 microns, $<2 \times 10^{-6}$ meters) in size on standard particle size classifications]. In the present context, clay minerals,

which can be classified into various chemical groups, such as the silicate clay mineral groups are an important part of many soils, thus rendering the soil capable of having a high adsorption capacity for inorganic chemicals. Generally, no two clay minerals are the same and the adsorption capacity will vary accordingly.

Adsorption of an inorganic chemical on to a solid adsorbent, such as a clay mineral or any other mineral, is measured by a partition coefficient, which is the ratio of the concentration the inorganic chemical on the solid to the concentration of the chemical in the fluid (usually water) surrounding the solid:

$$K_d = C_{\text{solid}}/C_{\text{water}}$$

The concentration on the solid has units of mol/kg, and the concentration in the water is mol/L and, thus, the adsorption coefficient (K_d) has units of L/kg. Assuming a solid density of 1 kg/L, these units are often ignored. The adsorption coefficient will often depend on how much of the total mass of the particle is inorganic material. Thus, the adsorption coefficient can be corrected by the fraction of inorganic material (f_{om}) in the particles:

$$K_{\text{om}} = K_d/f_{\text{om}}$$

Adsorbed molecules are those that are resistant to washing with the same solvent medium in the case of adsorption from solutions. The washing conditions can thus modify the measurement results, particularly when the interaction energy is low. The exact nature of the bonding depends on the details of the chemical species involved, but the adsorption process is generally classified as physisorption (which is characteristic of weak van der Waals forces which can be attractive or repulsive) or chemisorption (which is characteristic of covalent bonding). It may also occur due to electrostatic attraction.

The ease of desorption of the inorganic is also an important consideration, because in the treatment of wastewaters, materials are used primarily as ion exchangers, while for *in situ* immobilization, the metals need to be irreversibly bound to the added adsorbent.

See also: Adsorption.

Physical Transformation Reactions – Dilution

Dilution is the process in which an inorganic chemical in an ecosystem becomes less concentrated and there is a decrease in the concentration of a solute in solution, usually simply by mixing with additional solvent (such as water). Dilution is also a reduction in the acidity or alkalinity of an inorganic chemical (gas, vapor, solution). To dilute a solution means to add more solvent without the addition of more solute. The resulting solution is thoroughly mixed to ensure that all parts of the solution are identical. Mathematically, dilution can be represented by a simple equation:

$$C_1 \times V_1 = C_2 \times V_2$$

In this equation, C_1 is the initial concentration of the solute, V_1 is the initial volume of the solution, C_2 is the final concentration of the solute, and V_2 is the final volume of the solution. However, this type of simple equation does not consider any solute-solvent interactions, solute-solute interactions, and solvent-solvent interactions.

Dilution of the chemical may reduce the risk to the floral and faunal species because the potential individual receptors are likely to be exposed to lower, less toxic concentrations of the hazard. However, the chronic effects associated with the dilution of a toxic inorganic chemical (or any chemical for that matter) to a less-concentrated form is extremely difficult to measure. By itself, however, dilution does not reduce the mass of the chemical but, rather, spreads the area of potential exposure to the chemical. In addition, some inorganic contaminants are believed hazardous (such as the always lethal potassium cyanide, KCN) even at levels that may be too dilute to be detected with standard field characterization equipment and techniques.

Physisorption

In contrast with chemisorption (chemical adsorption), physisorption (physical adsorption) is the phenomenon which leaves the chemical species of the adsorbate and surface intact. It is conventionally accepted that the energetic threshold separating the binding energy of physisorption from that of chemisorption is approximately 0.5 eV per adsorbed species.

Adsorption is the phenomenon marked by an increase in density of a fluid near the surface of a solid. In the case of gas adsorption, this happens when molecules of the gas occasion to the vicinity of the surface and undergo an interaction with it, temporarily departing from the gas phase. Molecules in this new condensed phase formed at the surface remain for a period of time, and then return to the gas phase. The duration of this stay depends on the nature of the adsorbing surface and the adsorptive gas, the number of gas molecules that strike the surface and their kinetic energy (or collectively, their temperature), and other factors (such as capillary forces, surface heterogeneities, etc.). Adsorption is by nature a surface phenomenon, governed by the unique properties of bulk materials that exist only at the surface due to bonding deficiencies.

See also: Absorption, Adsorption, Chemisorption.

Pile Burners

Pile burners consist of cells, each having an upper and a lower combustion chamber. Biomass fuel burns on a grate in the lower chamber, releasing volatile gases. The gases burn in the upper (secondary) combustion chamber, and pile burners must be shut down periodically to remove ash.

Pile burners represent the historic industrial method of wood combustion and typically consist of a two-stage combustion chamber with a separate furnace and boiler located above the secondary combustion chamber. The combustion chamber is separated into a lower pile section for primary combustion and an upper secondary-combustion section. Wood is piled approximately 3.3 m (10 ft) deep on a grate in the bottom section, and combustion air is fed upwards through the grate and inwards from the walls; combustion is completed in a secondary combustion zone using overfire air. The wood fuel is introduced either on top of the pile or through an underfeed arrangement using an auger. The underfeed arrangement gives better combustion control by introducing feed underneath the active combustion zone, but it increases system complexity and lowers reliability. Ash is removed by isolating the combustion chamber from the furnace and manually dumping the ash from the grate after the ash is cooled. Pile burners typically have low efficiencies (50% to 60%), have cyclic operating characteristics because of the ash removal, and have combustion cycles that are erratic and difficult to control. Because of the slow response time of the system and the cyclic nature of operation, pile burners are not considered for load-following operations. The advantage of the pile burner is its simplicity and ability to handle wet, dirty fuels.

See also: Combustion, Stoker Combustors.

Pipeline Corrosion

As in the fossil fuels industry, the transportation of gases and liquids (from alternative energy sources) by pipeline can cause corrosion to the pipeline. One of the common problems in multiphase flow transmission pipelines is metal corrosion. Corrosion is defined as the deterioration of material, usually a metal, due to its reaction with the environment or handling media. The cause of corrosion can be directly attributed to the impurities found in the produced gas, as well as the corrosive components that are by-produced. Because of the non-specificity of the components produced from a production well, some or all of these components may be active to create a corrosive environment in the pipelines.

Corrosion in multiphase systems is a complex phenomenon, including dependency on the partial pressure, temperature, pH, and concentration of corrosion products. Consequently, corrosion prediction requires substantial understanding of the simultaneous interaction of the many process variables that govern both flow and corrosion conditions.

An important aspect of maintaining pipeline performance is adequate control of corrosion both internally (caused by the flow components and their by-products) and externally (because of pipeline exposure to the soil and water). Pipeline corrosion can be inhibited by several means which are (i) the choice of corrosion-resistant metals, alloys, (ii) the injection of corrosion inhibitors, (iii) cathodic protection, and (iv) the use of external and/or internal protective coatings.

While corrosion control can be achieved by selection of an appropriate corrosion-resistant metal, operating considerations usually dictate that a high-efficiency corrosion control system be used. Protecting pipelines from corrosion is achieved internally by the injection of inhibitors to mitigate internal corrosion and externally by use of cathodic protection and/or a combination of coatings and cathodic protection (for buried or subsea pipelines).

See also: Pipeline Protective Coating, Pipeline Transportation.

Pipeline – Protective Coating

While cathodic protection has historically been employed as the sole corrosion control methodology for subsea gas production systems, the nature of multiphase pipelines is such that the combined use of protective coatings with cathodic protection is necessary to achieve the effective protection. In fact, protective coatings help control pipeline corrosion by providing a barrier against reactants such as oxygen and water. However, because all organic coatings are semipermeable to oxygen and water, coatings alone cannot prevent corrosion and so a combination of cathodic protection is often used.

Pipelines are often internally coated to minimize corrosion when lying in pipeline dumps prior to construction and to provide a smooth surface that reduces friction when fluids are in transit. It should be noted that the initial period in the life of a production well can be its most corrosive time due to the high partial pressure of the carbon dioxide. Therefore, it may be more economical to protect the multiphase pipelines from a young field.

The coating must be compatible with the commodity and should have suitable resistance to attack by the commodity as well as any contaminants, corrosives, or inhibitor associated with it. Coatings such as epoxies, plastics, or metallic compounds can be used for selected applications. The oldest and still used approach consists of hot-applied bituminous material wrapped with an appropriate covering. External coatings are used to reduce the value of the external current to an economic level by imposing a barrier of high electrical resistance between metal and its environment.

Pipelines are susceptible to both internal and external corrosion. Therefore, both internal and external monitoring of a pipeline are required for a complete assessment, thus providing the direction that will ensure proper utilization of materials and corrosion control methodologies. While traditional inspection and monitoring techniques may represent effective solutions for assessment of the condition and integrity of a pipeline, the sensitivity and accuracy of these methods may be inadequate for monitoring inhibitor performance. However, the field signature method (FSM) continuously monitors corrosion taking place at a given point on the subsea pipeline and remaining pipe wall thickness at any time. This information can be transferred immediately to the surface, allowing the operator to take immediate action. Compared with traditional corrosion monitoring methods, the FSM reduces costs, improves safety, and may reduce the required frequency of intelligent pigging. The method requires virtually no maintenance or replacement of consumables. Its service life equals that of the pipe itself. However, it is still a relatively new technique and experience is improving.

See also: Pipeline Corrosion, Pipeline Transportation.

Pipeline Transportation

Pipelines are a very convenient method of transport but are not flexible as the gas will leave the source and arrive at its (one) destination. Once the pipeline diameter is decided, the quantities of gas that can be delivered are fixed by the pressures, although an increase in the maximum quantity can be achieved by adding compressors along the line, extra pipe in the form of loops, or by increasing the average pipeline pressure. However, if the pipeline has to be shut

down, the production and receiving facilities, be it gas reservoir, processor, or refinery, often also have to be shut down because gas cannot be readily stored, except perhaps by increasing the pipeline pressure by some percentage.

Pipeline pressures (onshore) usually operate under pressure at 700 to 1,100 psi (although 4,000 psi lines are in operation), and offshore pipelines operate under pressures on the order of 1,400 to 2,100 psi. The pressure does depend on the material of construction and the age of the pipe, and the high operating pressure reduces the volume of the natural gas being transported (by up to 600 times), as well as providing propellant force to move the natural gas through the pipeline. Pipeline installation costs vary but generally cost several million dollars (US) per mile depending on the terrain plus compressor stations. Sub-sea lines over 2,000 miles have, until recently, been regarded as uneconomic, because of the sub-sea terrain making pipeline installation and maintenance expensive and any recompression along the route difficult, but changes are in the air!

To ensure that the natural gas flowing through any one pipeline remains pressurized, compression of this natural gas is required periodically along the pipe. This is accomplished by compressor stations, usually placed at 40 to 100 mile intervals along the pipeline. The natural gas enters the compressor station, where it is compressed by a turbine, a motor, or an engine.

Turbine compressors gain their energy by using up a small proportion of the natural gas that they compress. The turbine itself serves to operate a centrifugal compressor, which contains a type of fan that compresses and pumps the natural gas through the pipeline. Some compressor stations are operated by using an electric motor to turn the same type of centrifugal compressor. This type of compression does not require the use of any of the natural gas from the pipe, but it does require a reliable source of electricity nearby. Reciprocating natural gas engines are also used to power some compressor stations. These engines resemble a large automobile engine, and are powered by natural gas from the pipeline. The combustion of the gas powers pistons on the outside of the engine, which serves to compress the natural gas.

In addition to compressing natural gas, compressor stations also usually contain some type of liquid separator, much like the ones used to dehydrate natural gas during its processing. Usually, these separators consist of scrubbers and filters that capture any liquids or other undesirable particles from the natural gas in the pipeline. Although natural gas in pipelines is considered to be *dry gas*, it is not uncommon for a certain amount of water and hydrocarbon derivatives to condense out of the gas stream while in transit. The liquid separators at compressor stations ensure that the natural gas in the pipeline is as pure as possible, and usually filters the gas prior to compression.

In addition to compressing natural gas to reduce its volume and push it through the pipe, metering stations are placed periodically along interstate natural gas pipelines. These stations allow pipeline companies to monitor and manage the natural gas in their pipes. The metering stations measure the flow of gas along the pipeline, and allow pipeline companies to monitor the natural gas as it flows along the pipeline. These metering stations employ specialized meters to measure the natural gas as it flows through the pipeline, without impeding its movement.

In the United States, there are essentially three major types of pipelines along the transportation route which are (i) the gathering system, (ii) the interstate pipeline, and (iii) the distribution system. The gathering system consists of low-pressure, low-diameter pipelines that transport raw natural gas from the wellhead to the processing plant. If natural gas from a particular well has a high sulfur content and a high carbon dioxide content (sour gas), a specialized sour gas gathering pipe must be installed. Sour gas is extremely corrosive and dangerous, thus its transportation from the wellhead to the sweetening plant must be done carefully.

In the United States, pipelines can also be characterized as interstate or intrastate. Interstate pipelines carry natural gas across state boundaries, in some cases clear across the country. Intrastate pipelines, on the other hand, transport natural gas within a particular state. In addition, natural gas pipelines are subject to regulatory oversight, which in many ways determines the manner in which pipeline companies must operate. The interstate natural gas pipeline network transports processed natural gas from processing plants in producing regions to those areas throughout the country with high natural gas requirements, particularly large, populated urban areas.

Interstate pipelines carry natural gas across state boundaries, in some cases clear across the country. Intrastate pipelines, on the other hand, transport natural gas within a particular state. In addition, natural gas pipelines are subject to regulatory oversight, which in many ways determines the manner in which pipeline companies must operate. The interstate natural gas pipeline network transports processed natural gas from processing plants in producing regions to those areas throughout the country with high natural gas requirements, particularly large, populated urban areas.

See also: See also: Pipeline Corrosion, Pipeline Protective Coating.

Pitch

Pitch is the nonvolatile, brown-to-black, semi-solid-to-solid viscous product from the destructive distillation of many bituminous materials or other organic materials (such as coal). It is also the name that is given (incorrectly) in the crude oil refining industry to the atmospheric residuum (atmospheric pitch) and vacuum residuum (vacuum pitch). The term should be carefully explained whenever it is in use.

On a scientific basis, pitch is considered to be a viscoelastic polymer which can be natural or manufactured, derived from crude oil, tar sand, or plant species. Various forms of pitch may also be called (incorrectly) tar, bitumen, or asphalt – in the refining industry, the vacuum residuum or the non-volatile material from various reactors (e.g., deasphalter pitch) is often referred to as pitch. Pitch produced from plants is also known as resin, and some products made from plant resin are also known as rosin.

Pitch was traditionally used to caulk the seams of wooden sailing vessels and to coat earthenware vessels for the preservation of liquids, such as wine. Pitch may also be used to waterproof wooden containers and in the making of torches. Crude oil-derived pitch is black in color, hence the adjectival phrase, pitch-black.

In the present context, pitch from any source can be subjected to pyrolysis to produce an array of products that fall into three categories: (i) gases, (ii) liquids, and (iii) solids. Also, heating (dry distillation, pyrolysis with simultaneous removal of distillate) of wood produces tar (the volatile constituents) and pitch (the non-volatile constituents) – the pitch is eventually decomposed further to produce char or charcoal.

While the terms tar and pitch are often used interchangeably – as indicated above – tar is more liquid and the volatile product of thermal decomposition, while pitch is considered a more non-volatile (often solid) distillation residue. Either tar or pitch can be decomposed further to produce fuel products.

See also: Refining, Tar Sand Bitumen.

Plant Fibers

Plant fibers (lignocellulosic fibers) are extracted from plants such as hemp and flax can replace cotton and polyester fibers in textile materials and glass fibers in insulation products.

Natural fibers can be classified according to their origin, thus: (i) the vegetable, or cellulose-base, class includes such important fibers as cotton, flax, and jute and (ii) the animal, or protein-base, fibers include wool, mohair, and silk.

The vegetable fibers can be divided into smaller groups based on their origin within the plant. Chemically, all vegetable fibers consist mainly of cellulose with varying amounts of such substances as pectin, hemicellulose, and lignin. Pectin is a structural acidic heteropolysaccharide contained in the cell walls of terrestrial plants – the main component of pectin is galacturonic acid, a sugar derived from galactose.

With the exception of mineral fibers, all natural fibers have an affinity for water in both liquid and vapor form. This strong affinity produces swelling of the fibers connected with the uptake of water, which facilitates dyeing in aqueous solutions.

See also: Biomass.

Plasma

The word *plasma* is used to describe a wide variety of macroscopically neutral substances containing many interacting free electrons and ionized atoms or molecules, which exhibit collective behavior due to the long-range coulomb forces. Not all media containing charged particles, however, can be classified as plasmas. For a collection of interacting charged and neutral particles to exhibit plasma behavior, it must satisfy certain conditions, or *criteria*, for plasma existence.

Matter is often classified in terms of four states: (i) gaseous, (ii) liquid, (iii) solid, and (iv) plasma. The basic distinction among the three common states of matter (gaseous, liquids, and solids) lies in the difference between the strength of the bonds that hold their constituent particles together. These binding forces are relatively strong in a

solid, weak in a liquid, and essentially almost absent in the gaseous state. Whether a given substance is found in one of these states depends on the *random kinetic energy* (thermal energy) of its atoms or molecules, i.e., on its temperature. The equilibrium between this particle thermal energy and the interparticle binding forces determines the state.

By heating a liquid or solid substance, the atoms or molecules acquire more thermal kinetic energy until they are able to overcome the binding potential energy. This leads to *phase transitions*, which occur at a constant temperature for a given pressure. The amount of energy required for the phase transition is called the *latent heat*.

If sufficient energy is provided, a molecular gas will gradually dissociate into an atomic gas as a result of collisions between those particles whose thermal kinetic energy exceeds the molecular binding energy. At sufficiently elevated temperatures, an increasing fraction of the atoms will possess enough kinetic energy to overcome, by collisions, the binding energy of the outermost orbital electrons, and an *ionized gas* or *plasma* results. However, this transition from a gas to a plasma is not a phase transition in the thermodynamic sense since it occurs gradually with increasing temperature.

See also: Plasma Arc Technology, Plasma Production.

Plasma Arc Technology

Plasma arc technology is a heating method that can be used in both pyrolysis and gasification systems. This technology was developed for the metals industry in the late nineteenth century.

Plasma arc technology uses high temperatures to break down the feedstock into elemental by-products. Plasma arc devices (plasma torches) can be one of two types: the transferred torch, and the non-transferred torch.

The transferred torch creates an electric field between an electrode (the tip of the torch) and the reactor wall or conducting slag bath. When the field strength is sufficiently high, an electric arc is created between the electrode and reactor (much like an automotive spark plug). The non-transferred torch creates the electric arc internal to the torch and sends a process gas (such as air or nitrogen) through the arc, where it is heated, and then leaves the torch as a hot gas. High temperatures are created in the ionized plasma (the plasma can reach temperatures of 3,875°C (7,000°F) and above; the non-ionized gases in the reactor chamber can reach 925 to 1,205°C (1,700 to 2,200°F), and the molten slag is typically around 1,650°C, 3,000°F).

See also: Plasma, Pyrolysis.

Plasma Gasifier

Plasma gasification is an extreme thermal process using plasma which converts organic matter into synthesis gas – primarily a mixture of hydrogen and carbon monoxide with slag remaining as a by-product. A plasma torch powered by an electric arc is used to ionize gas and is used commercially as a form of waste treatment as well as it has been tested for the gasification of biomass, industrial waste, refuse-derived fuel, and hazardous waste.

The high temperature and lack of oxygen prevents the formation of many toxic compounds such as furan derivatives, dioxin derivatives, nitrogen oxides, or sulfur dioxide in the flame itself. However, dioxin derivatives can be formed when the synthesis gas is cooled. A portion of the synthesis gas produced can be used as a feed to on-site turbines, which power the plasma torches and thus support the feed system.

Metals resulting from plasma pyrolysis can be recovered from the slag and eventually sold as a commodity. Inert slag produced from some processes is granulated and can be used in construction.

Plasma Production

A plasma can be produced by raising the temperature of a substance until a reasonably high fractional ionization is obtained. Under thermodynamic equilibrium conditions, the degree of ionization and the electron temperature are closely related. Plasmas in local thermodynamic equilibrium are found in many places in nature, as is the case for many astrophysical plasmas.

Plasmas can also be generated by ionization processes that raise the degree of ionization much above its thermal equilibrium value. There are many different methods of creating plasmas in the laboratory and, depending on the method, the plasma may have a high or low density, high or low temperature, it may be steady or transient, stable or unstable, and so on. In what follows, a brief description is presented of the most commonly known processes of *photoionization* and *electric discharge* in gases.

In the *photoionization* process, ionization occurs by absorption of incident photons whose energy is equal to, or greater than, the ionization potential of the absorbing atom. The excess energy of the photon is transformed into

kinetic energy of the electron-ion pair formed. For example, the ionization potential energy for the outermost electron of atomic oxygen is 13.6 eV, which can be supplied by radiation of wavelength smaller than approximately 91 nm, i.e., in the far ultraviolet. Ionization can also be produced by x-rays or gamma rays, which have much smaller wavelengths. The ionosphere of the Earth, for example, is a natural photoionized plasma.

In a *gas discharge*, an electric field is applied across the ionized gas, which accelerates the free electrons to energies sufficiently high to ionize other atoms by collisions. One characteristic of this process is that the applied electric field transfers energy much more efficiently to the light electrons than to the relatively heavy ions. The electron temperature in gas discharges is therefore higher than the ion temperature since the transfer of thermal energy from the electrons to the heavier particles is slow.

When the ionizing source is turned off, the ionization decreases gradually because of recombination until it reaches an equilibrium value consistent with the temperature of the medium. In the laboratory, the recombination usually occurs so fast that the plasma completely disappears in a small fraction of a second.

See also: Plasma.

Plasma Torch

A plasma torch (also known as a plasma arc, plasma gun, plasma cutter, or plasmatron) is a device for generating a directed flow of plasma which can be used for applications including plasma cutting, plasma arc welding, plasma spraying, and plasma gasification for waste disposal.

Thermal plasmas are generated in plasma torches by direct current (DC), alternating current (AC), radio frequency (RF), and other discharges. Direct current torches are the most commonly used and researched, because when compared to alternating current torches, the direct current torches offer (i) a more stable operation, (ii) better control, (iii) a minimum of two electrodes, (iv) lower electrode consumption, (v) slightly lower refractory wear, and (vi) lower power consumption.

In a direct current torch, the electric arc is formed between the electrodes (which can be made of materials such as copper, tungsten, graphite, and silver), and the thermal plasma is formed from the continual input of carrier/working gas, projecting outward as a plasma jet/flame (as can be seen in the adjacent image). Also, in direct current torches, the carrier gas can be, for example, either oxygen, nitrogen, argon, helium, air, or hydrogen and although termed such, it does not have to be a gas (thus, better termed a carrier fluid). However, the electrode materials and carrier fluids have to be specifically matched to avoid excessive electrode corrosion or oxidation (and contamination of materials to be treated), while maintaining ample power and function. Furthermore, the flow-rate of the carrier gas can be raised to promote a larger, more projecting plasma jet, provided that the arc current is sufficiently increased, and vice versa.

See also: Plasma, Plasma Arc Technology, Plasma Production.

Platform Chemicals

There are a number of potential platform chemicals that can be produced from agricultural feedstocks, including: citric acid, lactic acid, levulinic acid, succinic acid, and 1,3-propanediol, to name some of the more commonly discussed platforms. Each of these platforms has created interest in Europe and North America.

In the long term, North American industry intends to focus on using cheap lignocellulosic wastes to make sugars, which can be used as a platform for deriving various biochemical products. Under this scenario, three key factors must be present for the production of platform chemicals to be economically viable: access to large amounts of cheap lignocellulosic feedstocks; a ten-fold reduction in enzyme costs; and access to an existing ethanol and/or starch processing infrastructure that can act as a bridge for the production of other chemicals.

The development of biorefinery technology and the use of renewable resources are gaining importance in the chemical industry. The emphasis lies in the production of platform chemicals and synthesis gas from biomass (lignocellulosic feedstock).

Biomass as a renewable feedstock offers the opportunity to replace fossil feedstocks as a source of energy, materials, and chemicals. Sugars, oils, and other compounds in biomass can be converted into platform chemicals directly or as by-products from fuel product in processes analogous to the petrochemical industry.

Examples of these platform chemicals are ethanol (C2), glycerol (C3), fumaric acid (C4), xylitol (C5), and sorbitol (C6). These building block chemicals have a high transformation potential into new families of useful molecules. The use of biomass-derived chemicals represents an area with the potential for the development of a renewable feedstock-based technology platform. Improvements and innovations to existing biological and chemical processing of sugars will provide the opportunity for the production of high-value chemicals and products from biomass and reduced reliance on petrochemical-derived products.

See also: Synthesis Gas.

Plug Flow Digester

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen, used for industrial or domestic purposes to manage waste and/or to release energy.

Plug-flow digesters are suitable for ruminant animal manure that has a solids concentration of 11% to 13%. A typical design for a plug-flow system includes a manure collection system, a mixing pit, and the digester itself. In the mixing pit, the addition of water adjusts the proportion of solids in the manure slurry to the optimal consistency. The digester is a long, rectangular container, usually built below-grade, with an airtight, expandable cover.

New material added to the tank at one end pushes older material to the opposite end. Coarse solids in ruminant manure form a viscous material as they are digested, limiting solids separation in the digester tank. As a result, the material flows through the tank in a plug.

The average retention time (the time a manure plug remains in the digester) is 20 to 30 days. Anaerobic digestion of the manure slurry releases biogas as the material flows through the digester. A flexible, impermeable cover on the digester traps the gas. Pipes beneath the cover carry the biogas from the digester to an engine-generator set.

A plug-flow digester requires minimal maintenance. Waste heat from the engine-generator can be used to heat the digester. Inside the digester, suspended heating pipes allow hot water to circulate. The hot water heats the digester to keep the slurry at 25°C to 40°C (77°F to 104°F), a temperature range suitable for methane-producing bacteria. The hot water can come from recovered waste heat from an engine generator fueled with digester gas or from burning digester gas directly in a boiler.

See also: Aerobic Digestion, Anaerobic Digestion, Digesters.

Plutonium

Plutonium is an element that can be easily split to generate large amounts of energy, quickly and, therefore, is valuable as a fuel for nuclear reactors and as a key ingredient for nuclear weapons.

Plutonium is a heavy metallic element (more than twice as dense as iron). Its freshly prepared, uncorroded surface has a bright, silvery appearance, which tarnishes rapidly when exposed to air. While most metals are good conductors of electricity and heat, plutonium is not. Its electrical conductivity (ability to conduct electricity) and its thermal conductivity (ability to conduct heat) are both exceptionally low, only approximately one-hundredth as much as the conductivities of silver. The principal radiation from plutonium is the alpha particle. Alpha radiation is totally stopped by a single sheet of paper or even an inch of air. These alpha particles cannot penetrate the outer layer of one's skin. Therefore, plutonium outside the body is considered harmless. Even ingestion of these materials is of relatively low risk to humans. The greatest risk is in inhaling plutonium particles.

Plutonium is a radioactive element with an atomic number 94, and its position in the Periodic Table of the Elements (Table p-2) shows that it is the sixth member in the series of elements called the "actinides," of which actinium, atomic number 89, is the first member. Plutonium is also one of the transuranium elements, since it has an atomic number higher than that of uranium (number 92). Element 93 and those with higher numbers are man-made by transmutation (changing one element into another).

Plutonium has 15 known isotopes which range in atomic weight from plutonium-232 to plutonium-246 (²³²Pu to ²⁴⁶Pu). All of the isotopes are radioactive and decay spontaneously, according to various sequences, eventually forming a stable element such as bismuth or lead. Although all the plutonium isotopes are the same chemically, the rates

at which they disintegrate radioactively differ widely. The half-life of the plutonium-233 (^{233}Pu) isotope, for example, is approximately 20 minutes, while that of the plutonium-244 (^{244}Pu) isotope is approximately 76 million years. At present, plutonium-239 is the isotope of greatest importance because it is readily fissionable, has the relatively long half-life of 24,360 years, and can be produced in amounts large enough to be of practical use. The fissionable property of plutonium makes it an important source of nuclear energy. When a neutron strikes the nucleus of a plutonium-239 (^{239}Pu) atom and sticks to it (rather than glancing off), the nucleus splits (or fissions) to form two atoms of different elements, each having an atomic number approximately half that of plutonium – strontium and xenon or barium and krypton are examples. At the same time, two or more neutrons are ejected from the plutonium nucleus.

The fissionable property of plutonium makes it an important source of nuclear energy. When a neutron strikes the nucleus of a plutonium-239 atom and sticks to it (rather than glancing off), the nucleus splits (or fissions) to form two atoms of different elements, each having an atomic number approximately half that of plutonium. (Strontium and xenon or barium and krypton are examples.) At the same time, two or more neutrons are ejected from the plutonium nucleus.



These new neutrons may be absorbed by nuclei of other plutonium atoms, which then fission, in turn, and emit more neutrons. A nuclear chain reaction of rapidly increasing intensity is thus started and will continue until all the plutonium atoms are used up or until the neutrons are prevented from reacting with the plutonium atoms by being trapped in some other material or by escaping. During the fission process, an enormous amount of energy in the form of heat is released. This energy is equivalent to the difference between the mass of the reactants and the mass of the products of the reaction. In this instance, the reactants are the plutonium atom and a neutron, and the products are the two newly produced elements of lower atomic number and the newly produced neutrons.

See also: Periodic Table of the Elements.

Polar Cell

The polar cell is similar to the Hadley in that at about 60° , there is rising motion and movement toward the pole at upper levels with westerly motion. There is a subpolar low pressure system where storms and clouds develop. The air sinks at the poles producing the polar high, and at the surface, there is deflection to cause polar easterlies as the air moves from poles to the sub-polar low. A polar front separates cold air coming from the poles from milder air coming from midlatitudes, and the peaks of precipitation in the mid-latitudes are primarily produced by extra-tropical cyclones that develop along this front.

However, the smallest and weakest cells are the Polar Cells, which extend from between 60 and 70 degrees north and south, to the poles. Air in these cells sinks over the highest latitudes and flows out toward the lower latitudes at the surface.

It is important to recognize the existence of two separate planetary-scale circumpolar vortices: one in the stratosphere and the other troposphere. These vortices have different structure, seasonality, dynamics, and impacts on extreme weather. The tropospheric vortex is much larger than its stratospheric counterpart and exists year-round, whereas the stratospheric polar vortex forms in fall but disappears in the spring of each year. Both vortices can, in some circumstances, play a role in extreme weather events at the surface, such as cold air outbreaks, but these events are not the consequence of either the existence or gross properties of these two vortices. Rather, cold air outbreaks are most related to transient, localized displacements of the edge of the tropospheric polar vortex which may, in some circumstances, be related to the stratospheric polar vortex: but there is no known one-to-one connection between these phenomena.

See also: Atmosphere, Coriolis Force, Ferrel Cell, Hadley Cell, Walker Circulation, Wind Energy, Wind Power.

Pollutant

A pollutant is a substance or energy introduced into the environment that has undesired effects, or adversely affects the usefulness of a resource. A pollutant may cause long- or short-term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, health, or property values. Some pollutants are biodegradable and therefore will not persist in the environment in the long term but can still cause damage to the environment during the lifetime of the pollutant. A pollutant can also be a naturally-occurring material that is reintroduced into the environment in an amount that exceeds the naturally occurring amount in the environment.

Following from this definition, a primary pollutant is a pollutant that is emitted directly from a source. On the other hands, a secondary pollutant is a pollutant that is produced by interaction of a primary pollutant and with another chemical or by dissociation of a primary pollutant or other effects within a particular ecosystem (Table P-6).

Table P-6 Typical environmental pollutants.*

Pollutant	Description
Mercury (Hg)	A chemical element commonly known as quicksilver, a liquid under STP**.
Ozone (O ₃)	A pale blue gas with a distinctively pungent smell; formed from oxygen by the action of ultraviolet (UV) light and electrical discharges (lightning) within the atmosphere of the Earth; present in low concentrations throughout the atmosphere; the highest concentration is in the ozone layer of the stratosphere.
Particulate matter (PM)	Microscopic particles of solid or liquid matter suspended in the air; sources can be natural or anthropogenic.
Persistent organic chemicals (POPs)	Organic compounds that are resistant to environmental degradation by chemical, biological, and photolytic processes.
PAHs	Chemical compounds containing only carbon and hydrogen in the form of multiple fused aromatic rings; the simplest such chemicals are naphthalene and phenanthrene, having two fused aromatic rings, and the three fused aromatic rings, respectively.
VOCs****	Organic compounds that have a high vapor pressure at room temperature; the high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate (passes from liquid to gas) or sublimates (passes from solid to gas) and enter the surrounding air – often expressed as volatility.

*Listed alphabetically rather than by effect.

**Standard condition of temperature and pressure.

*** Polycyclic aromatic hydrocarbon derivatives; sometimes referred to as polynuclear aromatic hydrocarbon derivatives (PNAs).

****Volatile organic compounds

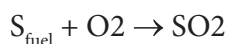
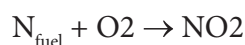
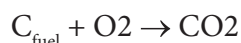
Human activities have released a large number of chemicals in the environment from industrial activities and domestic activities that are detrimental for health when they come into contact with human body. Many of these chemicals are toxic in nature and cause serious health problems in humans. Carcinogenic chemicals cause cancer where as many others cause various types of allergies in skin and respiratory system. Pesticides and a host of other chemicals enter the food chain through which it reaches human body and affects it adversely. Metals such as lead, mercury, and arsenic are introduced into the environment by industrial and domestics. These substances are toxic and cause various ailments when they enter the human body along with food or water.

For many pollutants, the atmosphere, the aquasphere, and the geosphere have the ability to sanitize (clean) themselves within hours or days, especially when the effects of the pollutant are minimized by the natural constituents of the ecosystem. For example, the atmosphere might be considered to be self-cleaning as a result of rain. However, removal of some pollutants from the atmosphere (such as sulfate derivatives and nitrate derivatives) by rainfall results in the formation of acid rain which can and will cause serious environmental damage to ecosystems within the aquasphere and the geosphere.

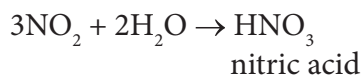
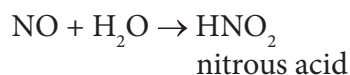
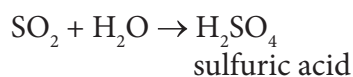
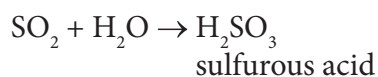
As a further aspect of this definition, the pollutant, by virtue of its name, has a detrimental effect on the environment, in part or in toto. Pollutants can also be subdivided into two classes which are (i) primary pollutants, and (ii) secondary pollutants:

Source → Primary pollutant → Secondary pollutant

Thus, a pollutant is a chemical which is emitted directly from the sources. In terms of atmospheric pollutants, the examples are carbon monoxide, carbon dioxide, sulfur dioxide (from which sulfur trioxide – in this case, a secondary pollutant is derived), and nitrogen oxides from combustion of carbonaceous fuels:



On the other hand, secondary pollutants are produced by the interaction of primary pollutants with another chemical or by the dissociation of a primary pollutant, or other effects within a particular ecosystem. Again, using the atmosphere as the example, the formation of the constituents of acid rain is an example of the formation of secondary pollutants:



In many cases, these secondary pollutants can have significant environmental effects, such as the formation of acid rain and smog.

Adsorption

The types of non-clay minerals and clays minerals in the soil give it the adsorption properties that are less desirable because of the ability of these minerals to trap potential pollutants within the soil.

Toxic substances including heavy metal(loid)s, such as arsenic (As), mercury (Hg), lead (Pb), cadmium (Cd), and chromium(VI) [Cr(VI)] and organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) (e.g., benzo[a]pyrene), persistent organic pollutants (POPs) (e.g., polychlorinated biphenyl) or emerging pollutants (e.g., per- and poly-fluoroalkyl substances, polybrominated biphenyls, etc. that present unique issues and challenges to environmental quality) have been detected in soils.

The adsorption and desorption of chemical pollutants in soils largely depend on (i) the type of mineral, (ii) the presence or absence of clay minerals, (iii) the pH, (iv) the redox conditions, and (v) the available chemical species. Inorganic ions, such as phosphate derivatives, HPO_4^{2-} , nitrate derivatives, NO_3^- , chloride derivatives, Cl^- , and sulfate derivatives, SO_4^{2-} and organic ligands, such as citrate, oxalate, fulvic, and dissolved organic carbon (DOC) can affect pollutant behavior in soils. Inorganic ions can influence adsorption through their interactions with metal(loid)s. For example, metal(loid)s complexed with such ions exhibit less sorption affinity to soils than free ions, but the free states of some ions (such as phosphate ions, PO_4^{3-}) in soil increase the net negative surface charge and therefore increase the sorption of cationic metal(loid)s. Soil organic constituents, such as soil organic matter, which is often estimated and expressed as soil organic carbon, play an important role in the sorption of soil pollutants. Some soil organic matter, such as humic substances, have a high affinity for metal cations. The heavy metal ion-binding ability of humic substances is attributed to the negative surface charge, particle size, and diffusion coefficient of humic acid as well as the content of oxygen-containing functional groups, including hydroxyl derivatives ($-\text{OH}$), carboxylic acid derivatives ($-\text{COOH}$), thiol derivatives ($-\text{SH}$), and aldehyde derivatives or ketone derivatives ($-\text{C}=\text{O}$). Another important process in soil is the microbial activity relative to the fate and transformation of pollutants. For example, the microbial degradation of hydrocarbon derivatives is experienced as the natural clean-up process of organic pollutants. Also, heavy metal(loid)s can be remediated using soil-grown plants (commonly accepted as phytoremediation), particularly with the microbial-assisted rhizosphere.

Organic pollutants can reach the soil either by purpose, such as pesticides and other agricultural chemicals, or incidentally through a variety of materials commonly used in agricultural practices, e.g., fertilizers and amendments. Once on the soil surface, the organic pollutant can be partially photo-decomposed and/or volatilized, and partially enter the soil or be transported to surface aquatic bodies by runoff and/or erosion. When in the soil, the pollutant can be subjected to partial or total chemical decomposition and/or biodegradation. The original pollutant and, possibly, its breakdown products may be adsorbed to soil organic and inorganic constituents, taken up by plant roots, and/or leached through the unsaturated zone eventually reaching the groundwater. All these processes are controlled by several factors including the physical and chemical properties of the pollutant and its breakdown products, the nature and thickness of the soil, the amount of water applied to the soil, and the type and extent of interactions between the pollutant and soil components.

The comment is often made that soil texture influences contaminant sorption phenomena and remediation processes in thermal desorption treatment. Also, contaminant removal was affected by soil texture. Although a soil could be all sand, all clay, or all silt, which is rare. Instead, most soils are a combination of the three. A clay loam texture soil, for example, has nearly equal parts of sand, silt, and clay and a soil with 15% w/w clay, 20% w/w silt, and 65% w/w sand has a sandy loam texture. Thus, soil texture is based on the relative proportions of each constituents in the soil of which non-clay minerals and clay minerals play important roles. In fact, the chemical and physical properties of a soil are related to texture. Particle size and distribution will also affect a capacity of the soil for holding water and nutrients. Fine-textured soils generally have a higher capacity for water retention, whereas sandy soils contain large pore spaces that allow leaching.

Thus, in order to determine the soil texture and to estimate the absorptive capacity of the soil, it is essential to know the constituents of the soil in terms of the amount of non-clay minerals (such as sand and silt) and the clay minerals (clay and often the amount of silt – silt can be fine sand, clay, or other material carried by running water and deposited as a sediment) in terms of the %w/w of sand, % w/w silt, and % w/w clay in the soil which can be estimated from the non-clay mineral and clay mineral content. However, this simplified approach to determining texture will may not have the required accuracy because of the ranges of the constituents and

if the soil contains a high amount of gypsum (CaSO_4) – soils that contain high amounts of gypsum (CaSO_4) typically show a pinkish-white hue. A more accurate test method (ASTM D7928) may be necessary using the soil triangle which is a diagram that illustrates how soils can be classified based on the percent of sand, silt, and clay in each.

Pollutant – Persistent

A persistent pollutant, like any chemical pollutant, can enter an ecosystem through the gas phase, the liquid phase, or solid phase and which can resist degradation and are mobile over considerable distances (especially in the gas phase or through transportation in river systems) before being re-deposited in a location that is remote to the location of their introduction into the ecosystem. Furthermore, pollutants can arise from various sources and can be present as vapors in the atmosphere or bound to (adsorbed on) the surface of soil or mineral particles and also have variable solubility in water.

Many persistent pollutants are currently (or were in the past) arose from the extensive use of fuels (from a variety of non-renewable and renewable sources) as well of agrochemicals (agricultural chemicals) such as pesticides, herbicides, and biocides, solvents, pharmaceuticals, and various industrial chemicals. Although some persistent pollutants arise naturally, for example from various biosynthetic pathways, most are products of human industry and tend to have higher concentrations and are eliminated more slowly. If not removed and because of their properties, persistent pollutants will bioaccumulate and have significant impacts on the flora and fauna of the environment. The most frequently used measure of the potential for bioaccumulations and the persistence of a compound in the environment are the result of the physicochemical properties (such as partition coefficients and reaction rate constants).

Solubility

From whatever the source of energy, chemicals are the most common type of contaminant in the aquasphere and they affect both surface and underground water bodies. Solvents and metals used in industries can pollute rivers and lakes. Weeds, insects, and fungi control in farms using pesticides is the other cause of soil contamination. The amount and dispersion of pollutants in the aquasphere is dependent upon the solubility of the pollutant in the water or the miscibility of the pollutant with water. In fact, many pollutants, through terrestrial runoff, direct discharge, or atmospheric deposition, end up in surface waters. In turn, rivers carry many of these pollutants to the sea. However, water quality varies from one location to the next depending on local geology, climate, biological activity, and human impact.

Even though nutrients are essential for plant and aquatic life, an excess of it is dangerous. Wastewater and fertilizers have a high content of nutrients required for plant growth. Consequently, they cause rapid and uncontrolled growth of vegetation and algae on the water surface when they end up in the water. This leads to clogging of water filters and contamination of drinking water. It also uses up all the oxygen leading to the destruction of marine life.

Also, aquatic microorganisms thrive on biodegradable substances, and when many of these chemicals are discharged into a waterway, the number of microorganisms increases. They use up all the oxygen in the water, and the depletion of oxygen leads to the death of aerobic microorganisms but promotes the growth of anaerobic organisms (eutrophication). In addition, certain anaerobic microorganisms contaminate the water by producing toxins such as sulfide derivatives and ammonia.

Some chemical contaminants do not dissolve in water, and, when suspended, they form a layer on the surface of the water, preventing oxygen penetration leading to oxygen depletion pollution. On the other hand, the particulate matter may settle at the bottom of the lake, ocean, or river, affecting the life on the floor of the river, lake, or ocean. In some cases, the material can comprise of harmful toxins.

In fact, the ability of a body of water to produce living material (the productivity of the water) results from a combination of chemical and physical factors. For example, water of low productivity generally is desirable for water supply or for swimming while relatively high productivity is required for the support of fish. Excessive productivity can result in choking by weeds and can cause odor problems. The growth of algae may become quite high in very productive waters, with the result that the concurrent decomposition of dead algae reduces oxygen levels in the water to low values (eutrophication).

When water pollution causes an algal bloom in a lake or marine environment, the proliferation of newly introduced nutrients stimulates plant and algae growth, which in turn reduces oxygen levels in the water. This scarcity of oxygen (eutrophication) suffocates plants and animals and can create dead zones in which the water is, to all intents and purposes, devoid of life. In certain cases, the harmful algal blooms can also produce neurotoxins that affect many forms of wildlife.

Moreover, the issue of eutrophication is due mainly to excessive, but inadvertent, introduction of domestic and industrial wastes, runoff from fertilized agricultural and urban areas, precipitation, and groundwater. The interaction of the natural processes within the lake with the artificial disturbance caused by human activities complicates the overall problem and leads to an accelerated rate of deterioration in lakes. Since a population increase necessitates an expanded utilization of lakes and streams, cultural eutrophication has become a major water resource problem throughout the world. Cultural eutrophication is reflected in changes in species composition, population sizes, and productivity in groups of organisms throughout the aquatic ecosystem.

Chemicals and heavy metals from industrial and municipal wastewater also contaminate waterways. These contaminants are toxic to aquatic life and often reduce the lifespan of an organism as well as the ability to reproduce, thereby accumulating in the food chain as predator eats prey. An example is the accumulation of mercury within various species of fish.

Life forms higher than algae and bacteria (e.g., fish) comprise a comparatively small fraction of the biomass in most aquatic systems. The influence of these higher life forms upon aquatic chemistry is minimal. However, aquatic life is strongly influenced by the physical and chemical properties of the body of water in which it lives.

Temperature, transparency, and turbulence are the three main physical properties affecting aquatic life. Low water temperatures result in slow biological processes, whereas high temperatures are fatal to most organisms. A difference of only a few degrees can produce large differences in the kinds of organisms present. Thermal discharges of hot water from power plants (cooling water) frequently kill temperature-sensitive fish while increasing the growth of fish and other species that are adapted to higher temperatures.

The transparency of water is particularly important in determining the growth of algae. Turbid water may not be very productive of biomass, even though it has the nutrients and optimum temperature. Turbulence is an important factor in mixing and transport processes in water. Some small organisms (plankton) depend upon water currents for their own mobility.

Water turbulence is largely responsible for the transport of nutrients to living organisms and of waste products away from them. It plays a role in the transport of oxygen, carbon dioxide, and other gases through a body of water and in the exchange of these gases at the water-atmosphere interface. Moderate turbulence is generally beneficial to aquatic life.

Biochemical oxygen demand, another important water-quality parameter, refers to the amount of oxygen utilized when the organic matter in a given volume of water is degraded biologically. A body of water with a high biochemical oxygen demand, and no means of rapidly replenishing the oxygen, obviously cannot sustain organisms that require oxygen. The degree of oxygen consumption by microbial oxidation of contaminants in water is called the biochemical oxygen demand (or biological oxygen demand).

The levels of nutrients in water frequently determine its productivity. Aquatic plant life requires an adequate supply of carbon (carbon dioxide, CO_2), nitrogen (nitrate, NO_3), phosphorus (orthophosphate, HPO_4^{2-}), and trace elements such as iron. In many cases, phosphorus is the limiting nutrient and is generally controlled in attempts to limit excess productivity. The salinity of water also determines the kinds of life forms present. Irrigation waters may pick up harmful levels of salt. Marine life obviously requires or tolerates salt water, whereas many freshwater organisms are intolerant of salt.

A majority of the important chemical reactions occurring in water, particularly those involving organic matter and oxidation-reduction processes, occur through bacterial intermediaries. Algae are the primary producers of biological organic matter (biomass) in water. Microorganisms are responsible for the formation of many sediment and mineral deposits; they also play the dominant role in secondary waste treatment.

Another example of waste control by oxidation involves oxidation of chemical waste materials in supercritical water. Supercritical water oxidation has been used to convert organic materials to carbon dioxide and is claimed to achieve destruction of 99.9%+ of chemicals such as polyols and amines that occur in liquid waste streams (Stadif, 1995).

See also: Aquasphere, Pollutant, Pollutant Adsorption, Pollutant – Persistent, Water.

Pollution

Pollution is the introduction of indigenous (beyond the natural abundance) and non-indigenous (artificial) gaseous, liquid, and solid contaminants into an ecosystem. The atmosphere and water and land systems have the ability to cleanse themselves of many pollutants within hours or days, especially when the effects of the pollutant are minimized by the natural constituents of the ecosystem. For example, the atmosphere might be considered to be self-cleaning as a result of rain. However, removal of some pollutants from the atmosphere (e.g., sulfates and nitrates) by rainfall results in the formation of acid rain that can cause serious environmental damage to ecosystems within the water and land systems. Pollutants, the elements of pollution, can be foreign substances or energies, or naturally occurring; when naturally occurring, they are considered contaminants when they exceed natural levels. Pollution is often classed as point source or nonpoint source pollution.

Sometimes, the term pollution is extended to include any substance when it occurs at such unnaturally high concentration within a system that it endangers the stability of that system. For example, water is innocuous and essential for life, and yet at high concentration, it could be considered a pollutant: if a person were to drink an excessive quantity of water, the physical system could be so overburdened that breakdown and even death could result. Another example is the potential of excessive noise to induce imbalance in the mental state of a person, resulting in malfunction and psychosis; this has been used as a weapon in warfare. The major forms of pollution by a refinery are: (i) air pollution, which is the release of chemicals and particulates into the atmosphere; common gaseous air pollutants include carbon monoxide and carbon dioxide, sulfur oxides, nitrogen oxides, particulate matter, and hydrocarbon derivatives, (ii) water pollution by the release of waste products and contaminants into surface runoff into river drainage systems, leaching into groundwater, liquid spills, wastewater discharges, eutrophication, and littering, and (iii) soil contamination occurs when chemicals are released by spill or underground leakage.

See also: Aquasphere, Atmosphere, Geosphere, Pollutant, Pollution Control.

Pollution Control

Pollution control is a term used in environmental management refers to control of emissions and effluents into air, water, or soil. Without pollution control, the waste products from consumption, heating, agriculture, mining, manufacturing, transportation, and other human activities, whether they accumulate or disperse, will degrade the environment. In the hierarchy of controls, pollution prevention and waste minimization are more desirable than pollution control.

In order to evaluate the need and use of for pollution control systems, it is necessary to estimate the mean concentration of pollutants in ecologically sensitive zones and preventing their dangerous levels through a control of emission rates of the relevant sources of the pollutants. The direct estimates use the solutions of pollution transport model allow performing complete analysis of ecological situation. On the other hand, the adjoint estimates depend explicitly on the number, positions, and emission rates of the sources and the initial distribution of pollutants in the region.

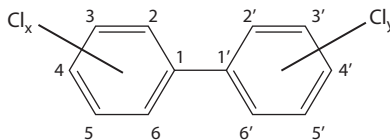
Each control strategy develops quantitative criteria with the aim to avoid violations of existing environmental norms through reductions in the emission rates of sources. Such criteria are designed taking into account (i) the processes of dispersion and transformation of pollutants, (ii) the number of point sources to control, and (iii) the locations of the sources.

See also: Aquasphere, Atmosphere, Gas Cleaning, Geosphere, Pollutant, Pollution.

Polychlorobiphenyls

Polychlorobiphenyls (PCBs, polychlorobiphenyl derivatives) are a class of chemical compounds in which as few as two and as many as ten (the maximum) chlorine atoms are attached to the biphenyl molecule. Monochlorinated

biphenyls (i.e., one chlorine atom attached to the biphenyl molecule) are often included when describing PCBs. The general chemical structure of chlorinated biphenyls:



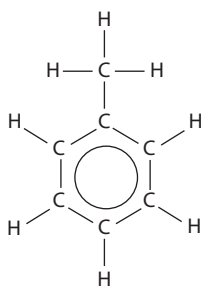
The benzene rings can rotate around the bond connecting them; the two extreme configurations are planar (the two benzene rings in the same plane) and the nonplanar in which the benzene rings are at a 90° angle to each other. The degree of planarity is largely determined by the number of substitutions in the ortho positions. The replacement of hydrogen atoms in the ortho positions with larger chlorine atoms forces the benzene rings to rotate out of the planar configuration. The benzene rings of non-ortho substituted polychlorobiphenyls, as well as mono-ortho substituted polychlorobiphenyls, may assume a planar configuration and are referred to as planar or coplanar congeners; the benzene rings of other congeners cannot assume a planar or coplanar configuration and are referred to as non-planar congeners.

The trade names of some commercial polychlorobiphenyl mixtures manufactured in other countries are Clophen (Germany), Fenclor (Italy), Kanechlor (Japan), and Phenoclor (France). The composition of commercial Clophen A-60 and Phenoclor DP-6 is similar to Aroclor 1260; that of Kanechlor 500 is similar to Aroclor 1254. Fenclor contains 100% decachlorobiphenyl.

Polycyclic Aromatic Hydrocarbons

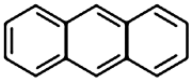
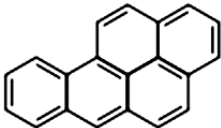
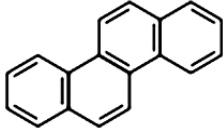
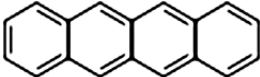
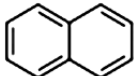
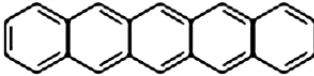
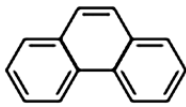
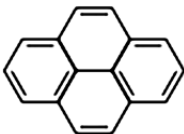
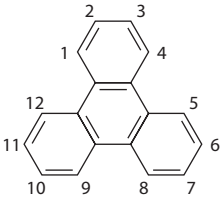
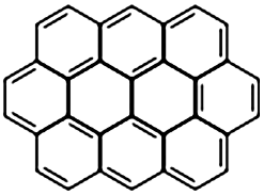
Polycyclic aromatic hydrocarbons (PAHs, also referred to as polynuclear aromatic hydrocarbons, PNAs) are a suite of compounds comprised of two or more condensed aromatic rings. They are found in many crude oil and alternate fuel mixtures, and they are predominantly introduced to the environment through natural and anthropogenic combustion processes.

Benzene (C_6H_6) is the simplest aromatic hydrocarbon and can have from one to six substituents attached to the central benzene core. An example of a benzene compound with just one substituent is toluene with a methyl group:



Polycyclic aromatic hydrocarbon derivatives are chemical compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents (Table P-7). They occur in crude oil and are produced as by-products of fuel oil burning. As a pollutant, they are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic.

Table P-7 Examples of polycyclic aromatic hydrocarbons.

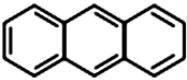
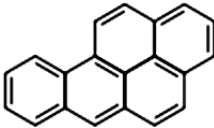
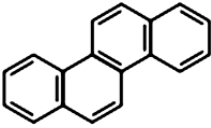
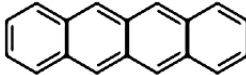
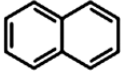
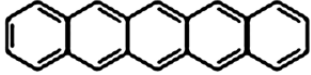
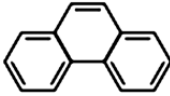
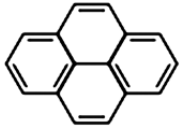
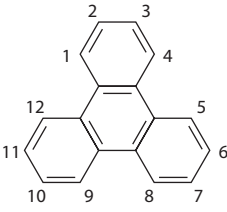
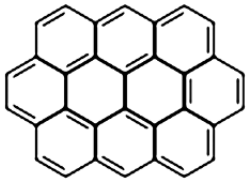
Chemical compound		Chemical compound	
Anthracene		Benzo(a)pyrene	
Chrysene		Coronene	
Corannulene		Naphthacene	
Naphthalene		Pentacene	
Phenanthrene		Pyrene	
Triphenylene		Ovalene	

See also: Peri-Condensed Aromatic Compounds, Polycyclic Compounds, Polynuclear Aromatic Compounds.

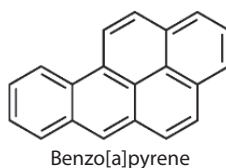
Polycyclic Compounds

In the field of organic chemistry, a polycyclic compound is an organic compound in which there are two or more closed rings of carbon atoms (Table P-8) and which can contain substructures of cycloalkanes (cycloparaffin hydrocarbons), aromatics, and other ring types that contain a heteroatoms such as nitrogen and/or oxygen and/or sulfur.

Table P-8 Examples of polycyclic aromatic compounds.

Chemical compound		Chemical compound	
Anthracene		Benzo[a]pyrene	
Chrysene		Coronene	
Corannulene		Naphthacene	
Naphthalene		Pentacene	
Phenanthrene		Pyrene	
Triphenylene		Ovalene	

The related term polycyclic organic matter (POM) defines a broad class of compounds that includes the polycyclic aromatic hydrocarbon compounds (PAHs, polynuclear aromatic compounds, PNAs), of which benzo[a]pyrene is a member.



Polycyclic organic matter is formed primarily from combustion and is present in the atmosphere in particulate form.

As a pollutant, polycyclic aromatic hydrocarbon derivatives are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic.

See also: Cycloparaffin Hydrocarbons, Heteroatom Compounds, Peri-Condensed Aromatic Compounds, Polycyclic Aromatic Hydrocarbons, Polynuclear Aromatic Compounds.

Polymer Waste

The disposal of the used polymeric materials is becoming a serious problem. Unlike natural polymers, most synthetic macromolecules cannot be assimilated by microorganisms. Although polymers represent slightly over 10% of total municipal waste, the problem of non-biodegradability is highlighted by overflowing landfills, polluted marine waters, and unsightly litter.

Total management of polymer wastes requires complementary combinations of biodegradation, incineration, and recycling. Biodegradation is the most desirable long-term future solution and requires intensive research and development before it becomes practical. On the other hand, incineration and recycling can become operational in a relatively short time for the improvement of the situation at present and in the near future.

Recycling of plastics that used to end up only at city landfills or incinerators is increasing and discarded plastic products and packaging make up a growing portion of Municipal Solid Waste (MSW).

Over the past two decades, recycling of plastics has dramatically increased. After years of predictions that plastics recycling would never be widespread because the processes were inefficient, too expensive, or not practical, the tide of waste headed to the landfill is slowly being turned.

A significantly important component of municipal solid waste is polymeric materials. Although polymer waste only accounts for 8.5% by mass of the total municipal solid waste disposed of in the United States, plastics represent over 28% v/v. Furthermore, most plastic wastes are not biodegradable and render a long-term waste management problem. The high volume-to-mass ratio and the inertness to biological reactions make the plastics and polymeric wastes the most important target for recycle, not for disposal. Polymeric wastes range from packaging materials used in the food industry to various parts in automobiles to high-density polyethylene (HDPE) containers for soft drinks and commercial liquids.

Within the next decades, the use of polymeric materials will continue to increase due to their versatility, functional values, and low energy requirements for production. The impetus to reuse the polymeric wastes instead of disposal in landfills is primarily due to the inability of polymers to rapidly degrade once dumped or buried at landfills.

There are a number of technologies available for the generation of fuel energy, either in gaseous or liquid form, from polymeric waste. These technologies include (i) pyrolysis, (ii) thermal cracking, (iii) catalytic cracking, and (iv) degradative extrusion as well as (v) partial oxidation. However, it is important to note that these are not the only processes available. As the technology advances, so do the processes used for the recovery of energy from wastes.

Pyrolysis of polymers is, by definition, the thermal decomposition of plastic waste back into oil or gas using heating processes under oxygen-starved or oxygen-deprived environment. This is the process typically used for waste-to-energy generation since it has several advantages. Besides being a proven technology, pyrolysis has a relatively good adaptability to fluctuations in the quality of the feedstock, simple to operate, and economical. In addition, refineries, which will utilize the chemically recycled polymers, already have pyrolysis units in operation.

Molten salts have also been successful at slightly lower operating temperatures. When the salts are used during a standard pyrolysis operation at 420°C (790°F), the gaseous fraction is minimized. This enables higher liquid and solid fractions to be recovered. While the nature of chemical reactions between the molten salts and polymeric waste is not yet completely understood, it does appear that production of a particular product mix is optimized by the presence of the salts. Typically, the recovered fractions consist of low-boiling oils, aromatic derivatives, paraffin waxes, and monomers. When pyrolysis utilizes molten salts, care must be taken to decrease the amount of corrosion and contamination to the pyrolysis chamber due to the salts.

Thermal cracking is similar to pyrolysis in that it is a high-temperature process. When polymeric wastes are cracked in an oxygen-free environment at temperatures above 480°C (900°F), a mixture of gas/liquid hydrocarbon is produced. At higher temperatures (650 to 760°C; 1,200 to 1,400°F), more of the gaseous product is generated. Conversely, at lower temperatures, up to 85% w/w of the product is a liquid hydrocarbon. Both the gas and liquid form of the converted mixed-polymeric waste can be utilized as a feed stream by crude oil facilities.

Catalytic cracking is similar to thermal cracking, but the primary difference is the addition of a catalyst to enhance the process. A typical catalytic cracker consists of two large reactor vessels: one vessel to react the feed over the hot catalyst and the other vessel to regenerate the spent catalyst by burning off carbon (fouled carbon on the catalytic surface) with air. Using two catalytic reactors enables the process to be run on a continuous basis.

Perhaps the most widely studied classification of catalysts for cracking operations is that of solid acid catalysts. The differences between the catalysts arise in the production of the coke and gas fractions. Formation of coke is not desirable since it causes catalytic deactivation by fouling and plugging the pore paths.

Regardless of the catalyst used, catalytic cracking, due to lower temperature operation, appears to be more technologically sound than pyrolysis. However, catalytic processes are often costlier than noncatalytic counterparts due to the costs involved in catalysts, catalytic reactors, and catalyst regeneration steps.

See also: Municipal Solid Waste, Waste, Refining.

Polynuclear Aromatic Compounds

A polynuclear aromatic (PNA) compound having two or more fused benzene rings, such as naphthalene and phenanthrene.

See also: Peri-Condensed Aromatic Compounds, Polycyclic Aromatic Hydrocarbons, Polycyclic Compounds

Pongamia Oil

Pongamia pinnata (Indian Beech Tree, Honge Tree, Pongam Tree, *Millettia Pinnata*) is a fast-growing evergreen tree which reaches 40 feet in height with up to a 55-foot spread, forming a broad, spreading canopy casting moderate shade. The six-to-nine-inch-long, pinnately compound, shiny dark green leaves are briefly deciduous, dropping for just a short period of time in early spring but being quickly replaced by new growth. Pongam is at its finest in the spring when the showy, hanging clusters of white, pink, or lavender, pea-like, fragrant blossoms appear, the clusters up to 10 inches long. The tree is believed to have originated in India and is native to a number of countries including India, Malaysia, Indonesia, Taiwan, Bangladesh, Sri Lanka, and Myanmar. It has also been naturalized in parts of eastern Africa, northern Australia, and Florida. Wherever it is grown, the wood (calorific value: 4,600 kcal/kg) is burned for cooking fuel. The thick oil from the seeds is used for illumination, as a kerosene substitute, and lubrication.

The seed oil (pongamia oil – other names for this oil include honge oil, kanuga oil, karanja oil, and pungai oil which has a high content of triglycerides) has been found to be useful in diesel generators, and, along with *Jatropha*, it is being explored in hundreds of projects throughout India and the third world as feedstock for biodiesel. It is especially attractive because it grows naturally through much of arid India, having very deep roots to reach water, and is one of the few crops well-suited to commercialization by countries that have large populations of rural poor. Several unelectrified villages have recently used pongamia oil, simple processing techniques, and diesel generators to create their own grid systems to run water pumps and electric lighting.

See also: Biodiesel, Transesterification, Vegetable Oil.

Porosity

The porosity (n) of a rock formation is the volume of voids in the formation divided to the total volume of the formations and is presented as a percentage. Thus:

$$\text{Porosity } (n) = (\text{volume of voids, } V_v) / (\text{total volume of the rock, } V_t)$$

The primary porosity is the inherent characteristic that is developed during the formation of the rock – examples are unconsolidated formations and sedimentary rocks have intergranular spaces. In basalts, the primary porosity is due to gas cavities, the lava tubes, and lava tunnels. The amount of pore space depends on the degree of compaction of the sediment (with compaction generally increasing with depth of burial), on the packing arrangement and shape of grains, on the amount of cementation, and on the degree of sorting. Typical cements are siliceous, calcareous or carbonate, or iron-bearing minerals. In consolidated rocks, the openings are primarily present as fractures, at joints, along bedding planes, and in the form of solution holes.

Secondary porosity is developed due to subsequent processes such as fracturing, jointing, and solution activities. In the igneous and metamorphic rocks as well as the hard sedimentary rocks, the porosity is secondary in nature.

The effective porosity, n_e , is the volume of pores that is available for transport of water, divided by the bulk volume. The effective porosity is slightly less than the porosity as part of the water that is molecularly bound to the pores or is stored in dead end pores does not participate in the flow. Porosity is a non-dimensional number, which could range from 0-1, it is often reported as a percentage (Table P-9). In the fractured rocks, the porosity depends upon the size of the individual fractures, joints, and other openings.

Table P-9 Porosity of different rock types.

Rock type	Range of porosity, %
Gravel	0.2-0.4
Sand	0.2-0.5
Silt	0.3-0.5
Clay	0.3-0.7
Fractured basalt	0.05-0.5
Karst limestone	0.05-0.5
Limestone, dolomite	0.0-0.2
Shale	0.0-0.2

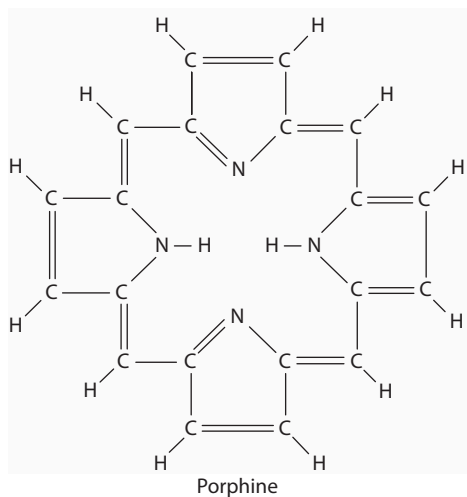
Sedimentary rocks and soils generally have the highest porosities, mostly from primary, while secondary contributes to fracturing and dissolution. Igneous and metamorphic rocks generally have low primary porosity, with sometimes-significant secondary porosity (fractures, especially in volcanic rocks). Rounded grains have smaller pore spaces between them in relation to irregularly shaped grains. Compaction results in reduction in porosity due to weight of overburden.

See also: Permeability.

Porphyryns

Porphyryns, which are complex derivatives of the basic material porphine, occur as part of the nitrogen-containing constituents of crude oil as well as bio-oil produced from certain types of biomass.

The porphyryns series is based on the pyrrole system. The porphyryns are actually based on a conjugated cyclic structure (porphine), which consists of four pyrrole rings linked together in the 2 and 5 positions by methine (=CH-) bridges:



Although porphine itself does not appear to exist in nature, structures based on this system are important to the existence of plant and animal life. In the animal kingdom, the porphine system occurs as hemoglobin (in the heme part of the molecule) in the red corpuscles of the blood and acts as an oxygen carrier to the lungs and to the body tissue. In the plant kingdom, porphyrin occurs in the chlorophyll found as the green coloring of leaves and stems which is essential for photosynthesis.

The porphyrin compounds are recognized as the degradation products of the chlorophyll (photosynthetic pigments of plants and some bacteria) and of the hemes and hematins, the respiratory pigments of both plants and animals. Most, if not all, of the porphyrin material in crude oils is completed with a metal, of which vanadium is the most important, followed by nickel, iron, as well as copper may also be present.

Porphyrins are a naturally occurring chemical species that exist in crude oil and usually occur in the non-basic portion of the nitrogen-containing concentrate. They are not usually considered among the usual nitrogen-containing constituents of crude oil, nor are they considered a metallo-containing organic material that also occurs in some crude oils. As a result of these early investigations, there arose the concept of porphyrins as biomarkers that could establish a link between compounds found in the geosphere and their corresponding biological precursors.

Porphyrins are derivatives of porphine [that consists of four pyrrole molecules joined by methine ($-\text{CH}=\text{}$) bridges]. The methine bridges establish conjugated linkages between the component pyrrole nuclei, forming a more extended resonance system. Although the resulting structure retains much of the inherent character of the pyrrole components, the larger conjugated system gives increased aromatic character to the porphine molecule. Furthermore, the imine functions ($-\text{NH}-$) in the porphine system allow metals such as nickel to be included into the molecule through chelation.

A large number of different porphyrin compounds exist in nature or have been synthesized. Most of these compounds have substituents other than hydrogen on many of the ring carbons. The nature of the substituents on porphyrin rings determines the classification of a specific porphyrin compound into one of various types according to one common system of nomenclature. Porphyrins also have well-known trivial names or acronyms that are often in more common usage than the formal system of nomenclature.

When one or two double bonds of a porphyrin are hydrogenated, a chlorin or a phlorin is the result. Chlorins are components of chlorophylls and possess an iso-cyclic ring formed by two methylene groups bridging a pyrrole-ring carbon to a methine carbon. Geological porphyrins that contain this structural feature are assumed to be derived from chlorophylls. Etioporphyrin derivatives are also commonly found in geological materials and have no substituents (other than hydrogen) on the methine carbons. Benzoporphyrins and tetrahydrobenzo-porphyrin derivatives also have been identified in geological materials. These compounds have either a benzene ring or a hydrogenated benzene ring fused onto a pyrrole unit.

Positron

The positron (sometimes referred to as the antielectron, the antiparticle, or the antimatter counterpart of the electron) has an electric charge of $+1 e$, a spin of $1/2$ (the same as the electron), and has the same mass as an electron. When a positron collides with an electron, destruction occurs, and if this collision occurs at a low energy level, it results in the production of two or more photons. A positron can be created by positron emission radioactive decay (through weak interactions), or by pair production from a sufficiently energetic photon which is interacting with an atom in a material.

More specifically, positrons are produced naturally in the β^+ decay of naturally occurring radioactive isotopes and by the interaction of gamma quanta (emitted by radioactive nuclei) with matter. In the radioactive decay process, unstable atomic nuclei due to too many protons relative to the number of neutrons and the nucleus decays to stable form by converting a proton to a neutron after which a positron is ejected to conserve electric charge. The positron annihilates with an electron, releasing two anti-colinear high-energy photons.

Antineutrinos are another kind of antiparticle produced by natural radioactivity (β^- decay). Positrons are also produced in gamma-ray flashes created by electrons accelerated by strong electric fields in the clouds. Antiparticles, of which the most common are positrons due to their low mass, are also produced in any environment with a sufficiently high temperature (mean particle energy greater than the pair production threshold).

Positron production from radioactive can be considered both artificial and natural production, as the generation of the radioisotope can be natural or artificial. Perhaps the best known naturally-occurring radioisotope which produces positrons is potassium-40 (^{40}K) potassium-40, a long-lived isotope of potassium which occurs as a primordial isotope of potassium.

See also: Electron, Radioactive Decay.

Possible Reserves

While probable reserves are those reserves of crude oil that are nearly certain but approximately which a slight doubt exists, possible reserves are those reserves of crude oil with an even greater degree of uncertainty related to recovery but about which there is some information. An additional term potential reserves is also used on occasion; these reserves are based upon geological information related to the types of sediments where such resources are likely to occur and they are considered to represent an educated guess (Table P-10).

Table P-10 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

There are the so-called undiscovered reserves, which are a little more than figments of imagination! The terms undiscovered reserves or undiscovered resources should be used with caution, especially when applied as a means of estimating reserves of crude oil reserves. The data are very speculative and are regarded by many energy scientists as having little value other than unbridled optimism.

Post-Combustion Cleaning

Post-combustion cleaning involves removal of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and/or particulates from the flue gas after it exits the boiler. Conventional technology (wet scrubbers) uses limestone or lime (and in some cases other alkaline agents) to remove sulfur pollutants from the flue gas before it exits the stack. Such processes can be plagued by corrosion and plugging and also produce a wet waste product (sludge) which has high disposal costs.

Advanced post-combustion cleaning technologies encompass two approaches which are (i) using the existing flue gas ductwork to inject a sorbent and (ii) inserting one or more separate vessels into the downstream ductwork where pollutant absorbents are added. These advanced technologies offer several advantages over conventional technologies such as (i) regeneration of the sulfur-absorbing chemical, (ii) increased residence time with the sulfur absorbent, (iii) reduced physical size requirements, and (iv) a dry, environmentally benign, waste product that may have commercial value.

In-duct sorbent cleaning occurs out, as the name indicates, inside the ductwork leading from the boiler to the smokestack. Sulfur dioxide absorbers (e.g., hydrated lime) are sprayed into the center of the duct. By controlling the humidity of the flue gas and the spray pattern of the sorbent, 50 to 70% of the sulfur dioxide can be removed and the reaction produces dry particles that can be collected downstream. In-duct sorbent injection is an attractive option for retrofitting smaller, older plants where space requirements might be limited.

When separate vessels are used, one or more process chambers are inserted in the flue gas ductwork, and various sorbents are injected to remove the pollutants. The separate vessels provide a longer residence time for the absorbent

to react with the gas, and pollutant capture is greater. This approach has the potential of capturing more than 90% of the pollutants. Technologies such as the spray dryer and selective catalytic reduction represent approaches that use separate vessels.

See also: Gas Cleaning Gas Processing, Gas Treating.

Potatoes

Potatoes are somewhat lower in total carbohydrates than sweet potatoes; thus, alcohol yields would be less even if total yields were similar.

Potatoes are potentially a lucrative source of biofuel. Corn has been the biofuel crop of choice, for two reasons which are (i) corn is energy-rich and (ii) corn is abundant. However, as biofuel gained in popularity, it created a problem: a lack of corn to actually eat.

Potatoes have all the handling advantages of sweet potatoes and are easier to establish, since seed pieces rather than transplants are used. The technology for making alcohol from potatoes is well developed, and this crop is worthy of consideration in areas where high yields are possible.

Sweet potatoes have been shown to yield two to three times as much carbohydrate for fuel ethanol production as field corn grown in the same areas. In fact, the sweet potato carbohydrate yields approached the lower limits of those produced by sugarcane, the highest-yielding ethanol crop. Sweet potatoes may also be a viable renewable fuel alternative as biofuel source.

See also: Biomass.

Potential Reserves

The term potential reserves is used on occasion to indicate reserves that are based upon geological information related to the types of sediments where such resources are likely to occur and they are considered to represent an educated guess (Table P-11).

Table P-11 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

The term inferred reserves is also commonly used in addition to, or in place of, potential reserves. Inferred reserves are regarded as of a higher degree of accuracy than potential reserves, and the term is applied to those reserves that are estimated using an improved understanding of reservoir frameworks. The term also usually includes those reserves that can be recovered by further development of recovery technologies.

Potential reserves are also those reserves where the relationship between the market price for the resource and the amount of the resource that can be profitably extracted at that price. The higher the price, the greater the potential reserves.

Potential reserves are also those reserves where the relationship between the market price for the resource and the amount of the resource that can be profitably extracted at that price. The higher the price, the greater the potential reserves.

See also: Reserves.

Pour Point

The pour point of a liquid fuel is the lowest temperature at which the fuel will pour or flow under prescribed conditions. When compared to reservoir temperature, it is an indication of whether or not the oil is pumpable without the input of additional heat energy. Also, the pour point is the minimum temperature of a liquid, particularly a lubricant, after which, on decreasing the temperature, the liquid ceases to flow.

It is also useful to note that failure of oil to flow at the pour point may also be due to the effect of viscosity or the previous thermal history of the specimen. Therefore, the pour point may give a misleading view of the handling properties of the oil. Additional fluidity or pumpability tests may also be undertaken. An approximate range of pour point can be observed from the upper and lower pour point of the sample.

The pour point test was originally applied to crude oil to crude oil products that had a high wax content. More recently, the pour point, like the viscosity, is determined principally for use in pumping and pipeline design calculations. Difficulty occurs in these determinations with waxy fuels that begin to exhibit irregular flow behavior when wax begins to separate. These fuels possess viscosity relationships that are difficult to predict in pipeline operation. In addition, some waxy fuels are sensitive to heat treatment that can also affect their viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy crude oils. At the present time, long crude oil pipelines and the increasing production of waxy crude oils make an assessment of the pumpability of a wax-containing crude oil through a given system a matter of some difficulty that can often only be resolved after field trials.

To measure the pour point, the sample is cooled inside a cooling bath to allow the formation of wax crystals. At approximately 9°C (16°F) above the expected pour point, and for every subsequent 3°C (5°F), the test jar is removed and tilted to check for surface movement. When the specimen does not flow when tilted, the jar is held horizontally for 5 seconds. If it does not flow, 3°C (5°F) is added to the corresponding temperature and the result is the pour point temperature.

Precipitation

Precipitation follows one of two processes which are (i) collision-coalescence which occurs when water droplets collide and combine together to form larger droplets as larger droplets are pulled earthward by gravity and updrafts can recycle the droplets through the cloud, increasing droplet size, and (ii) Bergeron processes occur where temperatures fall below freezing and pure water droplets remain liquid until supercooled to temperatures of more than -20°C (-4°F) at which time miniature ice crystals or supercooled water droplets may act as condensation surfaces. However, the density of water vapor in the air prior to saturation is slightly less adjacent to ice surfaces than water surfaces. Consequently, water vapor is added to the growing ice crystals (by deposition) rather than the water droplets. Eventually, precipitation of ice or snow occurs unless the frozen water is warmed as it falls through the atmosphere, resulting in rain.

See also: Acid Rain, Chemical Precipitation, Supercritical Fluid Precipitation.

Pressure Swing Adsorption

Pressure swing adsorption is generally the purification method of choice for steam reforming units because of its production of high purity hydrogen and is also used for purification of refinery off-gases, where it competes with membrane systems.

Pressure-swing adsorption units use beds of solid adsorbent to separate impurities from hydrogen streams leading to high-purity high-pressure hydrogen and a low-pressure tail gas stream containing the impurities and some of the hydrogen. The beds are then regenerated by depressurizing and purging. Part of the hydrogen (up to 20% v/v) may be lost in the tail gas.

Pressure swing adsorption is generally the purification method of choice for steam reforming units because of its production of high purity hydrogen and is also used for purification of refinery off-gases, where it competes with membrane systems.

Many hydrogen plants that formerly used a wet scrubbing process for hydrogen purification are now using the *pressure-swing adsorption* (PSA) concept for purification. The pressure swing adsorption process is a cyclic process that uses beds of solid adsorbent to remove impurities from the gas and generally produces higher purity hydrogen (99.9 volume percent purity compared to less than 97 volume per cent purity). The purified hydrogen passes through the adsorbent beds with only a tiny fraction absorbed, and the beds are regenerated by depressurization followed by purging at low pressure.

When the beds are depressurized, a waste gas (or *tail gas*) stream is produced and consists of the impurities from the feed (carbon monoxide, carbon dioxide, methane, and nitrogen) plus some hydrogen. This stream is burned in the reformer as fuel and reformer operating conditions in a pressure swing adsorption plant are set so that the tail gas provides no more than approximately 85% of the reformer fuel. This gives good burner control because the tail gas is more difficult to burn than regular fuel gas and the high content of carbon monoxide can interfere with the stability of the flame. As the reformer operating temperature is increased, the reforming equilibrium shifts, resulting in more hydrogen and less methane in the reformer outlet and hence less methane in the tail gas.

Many hydrogen plants that formerly used a *wet scrubbing* process for hydrogen purification are now using the *pressure-swing adsorption* (PSA) for purification. The pressure swing adsorption process is a cyclic process that uses beds of solid adsorbent to remove impurities from the gas and generally produces higher purity hydrogen (99.9 volume percent purity compared to less than 97 volume percent purity). The purified hydrogen passes through the adsorbent beds with only a tiny fraction absorbed, and the beds are regenerated by depressurization followed by purging at low pressure.

When the beds are depressurized, a waste gas (or *tail gas*) stream is produced and consists of the impurities from the feed (carbon monoxide, carbon dioxide, methane, and nitrogen) plus some hydrogen. This stream is burned in the reformer as fuel and reformer operating conditions in a pressure swing adsorption plant are set so that the tail gas provides no more than approximately 85% of the reformer fuel. This gives good burner control because the tail gas is more difficult to burn than regular fuel gas and the high content of carbon monoxide can interfere with the stability of the flame. As the reformer operating temperature is increased, the reforming equilibrium shifts, resulting in more hydrogen and less methane in the reformer outlet and hence less methane in the tail gas.

See also: Gas Cleaning.

Pressurized Water Reactor

The pressurized water reactor (PWR) is a common nuclear power reactor design in which very pure water is heated to a high temperature by fission, kept under high pressure to prevent it from boiling, and converted to steam by a steam generator rather than by boiling, as in a boiling water reactor. The resulting steam is used to drive turbines, which activate the generators to produce electrical power.

More specifically by stages, in a typical commercial pressurized water reactor, the following process occurs: (i) the core inside the reactor vessel creates heat, (ii) pressurized water in the primary coolant loop carries the heat to the steam generator, (iii) inside the steam generator, heat from the primary coolant loop vaporizes the water in a secondary loop, producing steam, and (iv) the steam line directs the steam to the main turbine, causing it to turn the turbine generator, which produces electricity.

The unused steam is exhausted to the condenser, where it is condensed into water which is pumped out of the condenser with a series of pumps, reheated, and pumped back to the steam generator. The core of the reactor contains fuel assemblies that are cooled by water circulated using electrically powered pumps. These pumps and other operating systems in the plant receive their power from the electrical grid. If offsite power is lost, emergency cooling water is supplied by other pumps, which can be powered by onsite diesel generators. Other safety systems, such as the containment cooling system, also need electric power. A pressurized water reactor may contain between 150 and 200 fuel assemblies.

Pressurized water reactors have advantages over the other light water reactors and earlier generation nuclear sites. One major advantage of this reactor is that it is easy to operate because less power is being produced as the heat increases. In addition, the core of the reactor contains less fissile material, decreasing the chances of additional fission events to occur, making the reactor safer and more controllable. In other words, then reactor contains less

fissile material than is required for the reactor to go prompt critical. Also, the most advantageous element of the pressurized water reactor is the turbine cycle. Since the primary and secondary loops are separate, water can never be contaminated by radioactive material in the main system loop. Conclusively, the water from the primary and secondary loops will never touch or mix, so there is no chance for contamination.

See: Nuclear Reactor – Pressurized Water Reactor.

Primary Biomass Feedstock

Primary biomass is biomass that is harvested or collected from the field or forest where it is grown and includes all terrestrial plants now used for food, feed, fiber, and fuel wood. All plants in natural and conservation areas (as well as algae and other aquatic plants growing in ponds, lakes, oceans, or artificial ponds and bioreactors) are also considered primary biomass.

Examples of primary biomass feedstocks currently being used for bioenergy include grains and oilseed crops used for transportation fuel production, plus some crop residues (such as orchard trimmings and nut hulls) and some residues from logging and forest operations that are currently used for heat and power production. In the future, it is anticipated that a larger proportion of the residues inherently generated from food crop harvesting, as well as a larger proportion of the residues generated from ongoing logging and forest operations, will be used for bioenergy. Additionally, as the bioenergy industry develops, both woody and herbaceous perennial crops will be planted and harvested specifically for bioenergy and product end-uses.

Primary biomass is produced directly by photosynthesis and includes all terrestrial plants now used for food, feed, fiber, and fuelwood. All plants in natural and conservation areas (as well as algae and other aquatic plants growing in ponds, lakes, oceans, or artificial ponds and bioreactors) are also considered primary biomass. However, only a small portion of the primary biomass produced will ever be harvested as feedstock material for the production of bioenergy and bioproducts.

Primary biomass feedstocks are thus primary biomass that is harvested or collected from the field or forest where it is grown. Examples of primary biomass feedstocks currently being used for bioenergy include grains and oilseed crops used for transportation fuel production, plus some crop residues (such as orchard trimmings and nut hulls) and some residues from logging and forest operations that are currently used for heat and power production. In the future, it is anticipated that a larger proportion of the residues inherently generated from food crop harvesting, as well as a larger proportion of the residues generated from ongoing logging and forest operations, will be used for bioenergy. Additionally, as the bioenergy industry develops, both woody and herbaceous perennial crops will be planted and harvested specifically for bioenergy and bioproducts' end-uses.

See also: Biofuel, Biomass, Secondary Biomass.

Primary Gasification

Gasification is the thermal conversion of organic matter by partial oxidation into a gaseous product called synthesis gas which consists predominantly of hydrogen (H_2), carbon monoxide (CO), and small amounts of methane (CH_4), water vapor (H_2O), carbon dioxide (CO_2), nitrogen (N_2), and tar. The oxidant used for the gasification process can be air (hence, the occurrence of nitrogen in the gaseous product), pure oxygen, steam, or a mixture of these gases.

Air-based gasifiers typically produce a product gas containing a relatively high concentration of nitrogen with a low heating value. Oxygen and steam-based gasifiers produce a product gas containing a relatively high concentration of hydrogen and carbon monoxide, with a higher heating value. A significant amount of char is always produced in gasification which needs to be further processed and/or burned.

On the other hand, primary gasification is the initial step in the gasification process and involves thermal decomposition of the raw feedstock via various chemical processes and many schemes involve pressures ranging from atmospheric to 1,000 psi. Air or oxygen may be admitted to support combustion to provide the necessary heat. The product is usually a low heat-content (low-Btu) gas ranging from a carbon monoxide/hydrogen mixture to

mixtures containing varying amounts of carbon monoxide, carbon dioxide, hydrogen, water, methane, hydrogen sulfide, nitrogen, and typical products of thermal decomposition such as tar (themselves being complex mixtures, hydrocarbon oils, and phenols).

A solid char product may also be produced, and may represent the bulk of the weight of the original feedstock. This type of coal being processed determines (to a large extent) the amount of char produced and the analysis of the gas product.

See also Gasification, Secondary Gasification.

Primary Wood-Using Mill

A primary wood-using mill is a mill that converts round wood products into other wood products; common examples are sawmills that convert saw logs into lumber and pulp mills that convert pulpwood round wood into wood pulp.

See also: Wood, Logs and Woodchips.

Probable Reserves

Probable reserves are those reserves of crude oil that are nearly certain but about which a slight doubt exists (Table P-12).

Table P-12 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Possible reserves are those reserves of crude oil with an even greater degree of uncertainty relayed to recovery but about which there is some information. An additional term potential reserves is also used on occasion; these reserves are based upon geological information related to the types of sediments where such resources are likely to occur, and they are considered to represent an educated guess. Then, there are the so-called undiscovered reserves, which are little more than figments of the imagination! The terms undiscovered reserves or undiscovered resources should be used with caution, especially when applied as a means of estimating reserves of crude oil reserves. The data are very speculative and are regarded by many energy scientists as having little value other than an optimistic approach to reserve estimation.

Process Gas

The term process gas is often applied to gas produced in a refinery but can also be applied to a gas stream produced form alternate energy sources. The gas varies in composition and volume, depending on the origin of the process feedstock and process parameters. In fact, the terms refinery gas and petroleum gas are often used to identify liquefied petroleum gas or even gas that emanates as light ends (which are composed of gases and volatile liquids) from the atmospheric distillation unit or from any one of several other refinery processes. In the current context, the term process gas also includes the gaseous effluents from a biorefinery or from any biomass processing plant insofar as

similar constituents to those in refinery gas will also occur (but not to the same extent) from the thermal treatment of biomass.

In the refinery, process gas is produced in considerable quantities during the different refining processes and is used as fuel for the refinery itself and as an important feedstock for the production of petrochemicals. It consists mainly of hydrogen (H_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and olefins ($RCH=CHR^1$, where R and R^1 can be hydrogen or a methyl group) and may also include off-gases from petrochemical processes. Olefins such as ethylene ($CH_2=CH_2$, boiling point: $-104^\circ C$, $-155^\circ F$), propene (propylene, $CH_3CH=CH_2$, boiling point: $-47^\circ C$, $-53^\circ F$), butene (butene-1, $CH_3CH_2CH=CH_2$, boiling point: $-5^\circ C$, $23^\circ F$) *iso*-butylene ($(CH_3)_2C=CH_2$, $-6^\circ C$, $21^\circ F$), *cis*- and *trans*-butene-2 ($CH_3CH=CHCH_3$, boiling point: ca. $1^\circ C$, $30^\circ F$), and butadiene ($CH_2=CHCH=CH_2$, boiling point: $-4^\circ C$, $24^\circ F$) as well as higher boiling olefins are produced by various refining processes.

Also in the refinery, still gas is broad terminology for low-boiling hydrocarbon mixtures and is the lowest boiling fraction isolated from a distillation (*still*) unit in the refinery. If the distillation unit is separating light hydrocarbon fractions, the still gas will be almost entirely methane with only traces of ethane (CH_3CH_3) and ethylene ($CH_2=CH_2$). If the distillation unit is handling higher-boiling fractions, the still gas might also contain propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$), and their respective isomers. Fuel gas and still gas are terms that are often used interchangeably, but the term fuel gas is intended to denote the product's destination-to be used as a fuel for boilers, furnaces, or heaters.

A group of refining operations that contributes to gas production are the thermal cracking and catalytic cracking processes. The thermal cracking processes (such as the coking processes) produce a variety of gases, some of which may contain olefin derivatives ($>C=C<$). In the visbreaking process, fuel oil is passed through externally fired tubes and undergoes liquid phase cracking reactions, which result in the formation of lower-boiling fuel oil components. Substantial quantities of both gas and carbon are also formed in coking (both fluid coking and delayed coking) in addition to the middle distillate and naphtha. When coking a residual fuel oil or heavy gas oil, the feedstock is preheated and contacted with hot carbon (coke) which causes extensive cracking of the feedstock constituents of higher molecular weight to produce lower-molecular-weight products ranging from methane, via liquefied petroleum gas(es) and naphtha, to gas oil and heating oil. Products from coking processes tend to be unsaturated, and olefin-type components predominate in the tail gases from coking processes.

The various catalytic cracking processes, in which higher-boiling gas oil fractions are converted into gaseous products, various naphtha fractions, fuel oil, and coke by contacting the feedstock with the hot catalyst. Thus, both catalytic and thermal cracking processes, the latter being now largely used to produce chemical raw materials, result in the formation of unsaturated hydrocarbon derivatives, particularly ethylene ($CH_2=CH_2$), but also propylene (propene, $CH_3CH=CH_2$), isobutylene [isobutene, $(CH_3)_2C=CH_2$], and the *n*-butenes ($CH_3CH_2CH=CH_2$, and $CH_3CH=CHCH_3$) in addition to hydrogen (H_2), methane (CH_4) and smaller quantities of ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), and butane isomers [$CH_3CH_2CH_2CH_3$, $(CH_3)_3CH$]. Diolefins such as butadiene ($CH_2=CHCH=CH_2$) and are also present.

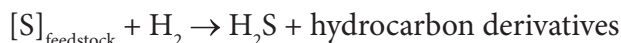
In a series of reforming processes, distillation fractions (as well as similar fractions from bio-oil processing) which include paraffin derivatives, and naphthene derivatives (cyclic non-aromatic) are treated in the presence of hydrogen and a catalyst to produce lower-molecular-weight products or are isomerized to more highly branched hydrocarbon derivatives. Also, the catalytic reforming process not only results in the formation of a liquid product of higher octane number but also produce substantial quantities of gaseous products.

The composition of these gases varies in accordance with process severity and the properties of the feedstock. The gaseous products are not only rich in hydrogen but also contain hydrocarbon derivatives from methane to butane derivatives, with a preponderance of propane ($CH_3CH_2CH_3$), *n*-butane ($CH_3CH_2CH_2CH_3$), and isobutane [$(CH_3)_3CH$]. Since all catalytic reforming processes require substantial recycling of a hydrogen stream, it is normal to separate reformer gas into a propane ($CH_3CH_2CH_3$) and/or a butane [$CH_3CH_2CH_2CH_3/(CH_3)_3CH$] stream, which becomes part of the refinery liquefied petroleum gas production, and a lower-boiling gaseous fraction, part of which is recycled.

A further source of refinery gas is produced by the hydrocracking process which is a high-pressure pyrolysis process carried out in the presence of fresh and recycled hydrogen. The feedstock is again heavy gas oil or residual fuel

oil, and the process is mainly directed at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again must be separated into lighter and heavier streams; any surplus recycle gas and the liquefied petroleum gas from the hydrocracking process are both saturated.

Both hydrocracker and catalytic reformer tail gases are commonly used in catalytic desulfurization processes. In the latter, feedstocks ranging from light to vacuum gas oils are passed at pressures on the order of 500 to 1,000 psi with hydrogen over a hydrofining catalyst. This results mainly in the conversion of organic sulfur compounds to hydrogen sulfide:



The process also has the potential to produce lower-boiling hydrocarbon derivatives by hydrocracking. Refinery gas, usually in more than one stream, is typically treated for hydrogen sulfide removal, and gas sales are usually on a thermal content (calorific value, heating value) basis with some adjustment for variation in the calorific value and hydrocarbon type.

See also: Refining.

Process Selection – Gas Treating

Each of the gas treating processes has advantages relative to the others for certain applications; therefore, in selection of the appropriate process, the following facts should be considered: (i) tail gas clean-up requirements, (ii) type and concentration of impurities in the sour gas, (iii) specifications for the residue gas, (iv) specifications for the acid gas, (v) temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered, (vi) volume of gas to be processed, (vii) hydrocarbon composition of the gas, and (viii) selectivity required for acid gas removal.

Decisions in selecting a gas treating process can many times be simplified by gas composition and operating conditions. High partial pressures (50 psi) of acid gases enhance the probability of using a physical solvent. The presence of significant quantities of high-boiling hydrocarbon derivatives in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating.

In general, the batch and amine processes are used for over 90% of all onshore wellhead applications. Amine processes are preferred when the lower operating cost, the chemical cost for this process, is prohibitive, and justifies the higher equipment cost. The key is the sulfur content of the feed gas where below 20 pounds of sulfur per day, batch processes are more economical, and over 100-pound sulfur per day amine solutions are preferred.

See also: Gas Cleaning.

Process Selectivity

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide while other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

See also: Gas Cleaning, Gas Processing.

Process Wastes

In any chemical production operation, the unit process operations that produce a variety of products from various feedstocks and feedstock blend and some of the wastes are present in air emissions, wastewater, or solid wastes.

Emissions are also created through the combustion of fuels, and as by-products of chemical reactions occurring when crude oil fractions are upgraded. A large source of air emissions is, generally, the process heaters and boilers that produce carbon monoxide, sulfur oxides, and nitrogen oxides, leading to pollution and the formation of acid rain.



Hence, there is the need for gas-cleaning operations on a production site so that such gases are cleaned from the gas stream prior to entry into the atmosphere.

In addition, some processes create considerable amounts of particulate matter and other emissions from catalyst regeneration or decoking processes. Volatile chemicals and hydrocarbon derivatives are also released from equipment leaks, storage tanks, and wastewaters. Other cleaning units such as the installation of filters, electrostatic precipitators, and cyclones can mitigate part of the problem.

Process wastewater is also a significant effluent from a number of refinery processes. Atmospheric distillation and vacuum distillation create the largest volumes of process wastewater, approximately 26 gallons per barrel of oil processed. Fluid catalytic cracking and catalytic reforming also generate considerable amounts of wastewater (15 and 6 gallons per barrel of feedstock, respectively). A large portion of wastewater from these three processes is contaminated with oil and other impurities and must be subjected to primary, secondary, and sometimes tertiary water treatment processes, some of which also create hazardous waste.

Wastes and by-products are produced by a number of processes. Residuals produced during refining can be but are not necessarily wastes. They can be recycled or regenerated, and in many cases do not become part of the waste stream but are useful products. For example, processes utilizing caustics for neutralization of acidic gases or solvent (e.g., alkylation, sweetening/chemical treating, and lubricating oil manufacture) create the largest source of residuals in the form of spent caustic solutions. However, nearly all of these caustics are recycled.

The treatment of wastewater from various processes generates the next largest source of residuals in the form of biomass sludge from biological treatment and pond sediments. Water treatment of oily wastewater also produces a number of sludge materials associated with oil-water separation processes. Such sludge is often recycled in the refining process and is not considered waste.

Producer Gas

Producer gas is mainly carbon monoxide with smaller amounts of hydrogen, methane, and variable amounts of nitrogen (Table P-13), obtained from partial combustion of coal or coke in air or oxygen, having a heat content of 110 to 160 Btu/ft³ (air combustion) or 400 to 500 Btu/ft³ (oxygen combustion).

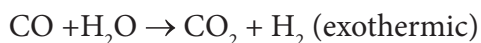
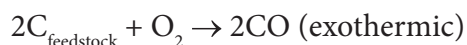
Table P-13 Typical composition of producer gas.

Source	Coal/coke	Wood
	-----Gas constituent-----	
	%, v/v	%, v/v
Hydrogen	20-22	12-15
Carbon monoxide	19-20	20-22
Carbon dioxide	12-14	9-11
Methane	2-5	2-3
Nitrogen	50-60	50-54

The gas is produced by blowing air and sometimes steam through an incandescent fuel bed (the process is self-heating). The reaction with air is exothermic, but insufficient air is added; hence, carbon monoxide is produced. Steam addition results in the formation of hydrogen by the water gas reaction. This is endothermic and hence balances out the exothermic air reaction. Producer gas is low calorific value and is hence typically used as an on-site fuel gas.

In the process – using coal as the example, of the carbonaceous feedstock – air is blown through an incandescent bed of coal. The amount of air is sufficient to maintain the process temperature but insufficient to complete the combustion reaction. The gas products is a mixture containing approximately 50% v/v nitrogen, from the air, 29% v/v carbon monoxide, due to incomplete combustion of the feedstock, and 4% v/v carbon dioxide, as well as sundry other products, including hydrocarbon derivatives. The heat content of the gas is low and, although not suitable for distribution to consumers, can be used on site as a fuel gas. In order to modify the product distribution, steam can be used in the process, and endothermic reactions (such as the water gas reaction) result in the formation of hydrogen.

Initially, the oxidation of the feedstock (coal) in the presence of the available oxygen occurs after which there is competition for oxygen between the carbon and the water gas reactions occur:



The ratio of steam and air may be used to modify the composition of the gas that is produced.

See also: Gasification.

Product Analysis

The chemical composition of products from alternate energy sources is, like the analysis of products from crude oil and other fossil fuel sources, complex but is a necessary part of product identification and quality. These two criteria make it essential that the most appropriate analytical methods are selected from a comprehensive list of methods and techniques that are used for the analysis of samples.

The analysis of a biomass-related feedstock for the percentages of carbon, hydrogen, nitrogen, oxygen, and sulfur is perhaps the first method used to examine the general nature, and perform an evaluation, of a feedstock. The atomic ratios of the various elements to carbon (i.e., H/C, N/C, O/C, and S/C) are frequently used for indications of the overall character of the feedstock. It is also of value to determine the amounts of trace elements, such as

vanadium, nickel and other metals, in a feedstock since these materials can have serious deleterious effects on catalyst performance during refining by catalytic processes.

Using bio-oil as the example, valuable information can be obtained from the true boiling point (TBP) curve which is a function of percent weight distilled and temperature, that is, a boiling point distribution. However, the boiling range does not convey much detail about chemical reactivity of the product. In addition to the boiling point distribution, it is possible to measure bulk physical properties, such as specific gravity and viscosity that have assisted in the establishment of certain empirical relationships for further processing from the *true boiling point* curve. Many of these relationships include assumptions that are based on experience with a range of feedstocks. However, the chemical aspects of refining feedstocks that contain different proportions of chemical species emphasize the need for more definitive data that would enable more realistic predictions to be made of feedstock behavior in upgrading operations. Any of the methods described herein might also be applied to the analysis of sample for environmental purposes.

The importance of chemical and physical properties is dependent upon the purity of the product. In the strictest sense, most gaseous, liquid, and solid products are complex chemical mixtures and typically contain hydrocarbon derivatives and non-hydrocarbon derivatives that confer properties on the mixture that may not be reflected in the composition. Therefore, it is necessary to apply various test methods to feedstocks and products to determine if the material is suitable for processing and (in the case of the products) for sale with a designated use in mind. The more common tests are introduced in the following sub-sections – these tests are presented in alphabetical order with no preference given to any particular test method.

Finally, an important aspect of feedstock analysis is the feedstock assay which is necessary because of the wide range of composition of, in the current context, the various biomass-related feedstocks.

An efficient and meaningful assay is derived from a series of test data that give an accurate description of feedstock quality and allow an indication of feedstock behavior during the conversion to products. The analyses are performed to determine whether each batch of a feedstock is suitable for conversion and upgrading purposes. The information required is feedstock dependent and to obtain the necessary information, two different analytical schemes are commonly used and these are: (i) a comprehensive assay and (ii) an inspection assay.

A comprehensive (or full) assay is more complex (as well as time-consuming and costly) than the inspection assay and is usually only performed only when a new batch (and previous untested) feedstock comes on stream, or when the inspection assay indicates that significant changes in the composition of the feedstock oil have occurred. Except for these circumstances, a comprehensive assay of a particular feedstock may involve at least the determination of (i) the elemental composition in terms of the carbon content, the hydrogen content, the nitrogen content, the oxygen content, the sulfur content, and the metals content as well as the types of metals. Other test methods (presented alphabetically but which are feedstock dependent and process dependent) that can be included in the comprehensive assay include (i) boiling point distribution, (ii) density, specific gravity, and API gravity, (iii) emulsion formation, (iv) evaporation, (v) fire point and flash point, (vi) fractionation, (vii) molecular weight, (viii) pour point, (ix) sulfur content, (x) surface tension and interfacial tension, (xi) total acid number, (x) viscosity, and (xi) water content. There are other test methods (such as, for example, the yield of carbon residue) designated necessary to understand properties and behavior of the crude oil under examination.

An inspection assay usually involves determination of several key bulk properties of the feedstock and the products (e.g., API gravity, sulfur content, pour point, and distillation range) as a means of determining if major changes in characteristics have occurred since the last comprehensive assay was performed. For example, a more detailed inspection assay might consist of the following tests: API gravity (or density or relative density), sulfur content, pour point, viscosity, salt content, water and sediment content, trace metals (or organic halides). The results from these tests with the archived data from a comprehensive assay provide an estimate of any changes that have occurred in the crude oil that may be critical to refinery operations. Inspection assays are routinely performed on all crude oils received at a refinery. The inspection assay tests discussed above are not exhaustive but are the ones most commonly used and provide data on the impurities present as well as a general idea of the products that may be recoverable. Other properties that are determined on an as needed basis include, but are not limited to, the following: (i) the vapor pressure (Reid method) for fuels, (ii) the total acid number, and (of somewhat lesser importance for many feedstocks and products) the aniline point (or mixed aniline point).

The *Reid vapor pressure* test method is a measure of the vapor pressure of volatile materials and differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space. The *acid number* is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample in this solvent to a green/green-brown end point, using p-naphtholbenzein indicator solution. The *strong acid number* is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared non-aqueous acidic buffer solution or a well-defined inflection point as specified in the test method. The *aniline point* (or *mixed aniline point*) is more applicable to pure hydrocarbon derivatives and is used to estimate the aromatic content of mixtures. Aromatic mixtures exhibit the lowest aniline points, and paraffin mixtures have the highest aniline points. Cycloparaffin derivatives and olefin derivatives exhibit values between these two extremes.

Therefore, the judicious choice of a feedstock to produce any given product (or products) is just as important as the selection of the product for any given purpose. Indeed, careful evaluation of the feedstock from physical property data is a major part of the initial study of any feedstock destined for conversion to produce a variety of products. Proper interpretation of the data resulting from the inspection of the feedstock (and the products) requires an understanding of the data from the test methods. In the following sections, an indication of the physical properties that may be applied to biomass feedstocks and process products is presented.

Boiling Point Distribution

Boiling range distribution data are used (i) to assess product quality before upgrading to a suitably sales product before purchase, (ii) to monitor product quality during transportation, (iii) to evaluate the product prior to upgrading, and (iv) to provide information for the optimization of the upgrading processes.

Traditionally, boiling range distributions of the various process products have been determined by distillation. Yield-on-feedstock data are still widely reported, thereby providing information on the yield of specific fractions obtained by distillation. To some extent in the laboratory, atmospheric and vacuum distillation techniques have largely been replaced by *simulated* distillation methods, which use low-resolution gas chromatography and correlate retention times to hydrocarbon boiling points.

From the point of view of feedstock and product analysis for environmental purposes, boiling range distributions provide an indication of volatility and component distribution. In addition, boiling range distribution data is also useful for the development of equations for predicting evaporative loss.

Density, Specific Gravity, and API Gravity

Density is the mass per unit volume of a substance. It is most often reported for oils in units of g/mL or g/cm³, and less often in units of kg/m³. Density is temperature-dependent. It is an important property of feedstocks and their respective products by providing the investigator(s) indications of whether or not the contaminant(s) will float on water or sink to the base of any water system.

Two density-related properties of feedstocks products are often used: (i) specific gravity and for fuels, (ii) the American Petroleum Institute (API) gravity. Specific gravity (*relative density*) is the ratio, at a specified temperature, of the feedstock and/or the product density to the density of pure water. The API gravity scale (presented as °API) arbitrarily assigns an API gravity of 10° to pure water. Thus:

$$^{\circ}\text{API} = [141.5/(\text{specific gravity at } 15.6^{\circ}\text{C}) - 131.5]$$

Typically, many organic feedstocks and products will float on water if the density of the material is less than that of the water. This behavior is typical of all crude oils and distillate products for both salt and fresh water.

Emulsion Formation

A water-in-oil emulsion is a stable dispersion of small droplets of water in oil, and when formed, these emulsions can have different characteristics from the parent crude feedstocks (if the feedstocks are liquid). This has important implications for the fate and behavior of any spilled products and any subsequent cleanup. It is desirable, therefore, to determine if the product is likely to form an emulsion, and if so, whether that emulsion is stable, and the physical characteristics of the emulsion.

However, it must be recognized that once spilled, the properties may be changed because emulsion formation and behavior are influenced by the oxidation of product constituents. The inclusion of polar functions such as hydroxyl groups (-OH) or carbonyl groups (>C=O) (a result of the oxidation process) causes an increase in the density of the emulsion (relative to the original unoxidized material) and with an increased propensity to form emulsions. As a result, the emulsion and sinks to various depths or even to the bottom of the water system, depending on the extent of the oxidation and the resulting density. This may give the erroneous appearance (leading to erroneous deductions with catastrophic consequences) that the spill (as evidenced from the material remaining on the surface of the water) is less than it actually was. The so-called *missing* product will undergo further chemical changes and eventually reappear on the water surface or on a distant shore.

Evaporation

Evaporation is the removal of the lower-boiling constituents from a product usually under ambient conditions or, in the current context, under the conditions prevalent at the spill site.

The evaporation rate and loss are of importance for all volatile constituents of the products of thermal and catalytic processes. While standard test methods such as those designated for distillation and vapor pressure determination are often used to determine evaporation properties, test methods for determining evaporation loss are available for higher-boiling products. Although not necessarily applicable to process products in general, evaporation loss data can be obtained at any temperature in the range from 93 and 316°C (200 and 600°F). Viscous samples can be analyzed using a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

It must also be recognized that as evaporation occurs, the density and viscosity of the residual product increase, thereby causing behavioral changes in the contaminant. Such changes could be reflected in an increase in adhesion of the contaminant constituents to the soil or rock.

Fire Point and Flash Point

The *fire point* is the lowest temperature, corrected to one atmosphere pressure (14.7 psi), at which the application of a test flame to a sample of a process product causes the vapor of the oil to ignite and burn for at least five seconds.

At any time after a spill of a product, fire should always be considered an imminent hazard. Related to fire point, the flash point is a measure of the tendency of the product to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that should be considered in assessing the overall flammability hazard of a spilled material.

The ignition temperature (sometimes called the *autoignition temperature*) is the minimum temperature at which the material will ignite without a spark or flame being present.

Also related to fire point, the flammability limits of vapor in air are an expression of the percent concentration in air (by volume) is given for the lower and upper limit. These values give an indication of relative flammability. The limits are sometimes referred to as *lower explosive limit* (LEL) and *upper explosive limit* (UEL).

The *flash point* of a product is the temperature to which the sample must be heated to produce a vapor/air mixture above the liquid fuel that is ignitable when exposed to an open flame under specified test conditions. Furthermore, the flash point is used as an index of fire hazard and is an extremely important factor in relation to the safety of spill cleanup operations. Low-boiling liquid fuels (from whatever the source) can be ignited under most ambient conditions and therefore pose a serious hazard when spilled.

Fractionation

Rather than quantifying a complex total feedstock or product mixture in the form of a single number, fractionation methods break the mixture into discrete fractions, thus providing data that can be used in a risk assessment and in characterizing product type and compositional changes such as may occur during weathering (oxidation). The fractionation methods can be used to measure both the volatile constituents and the extractable constituents.

In contrast to traditional methods that report a single concentration number for complex mixtures, the fractionation methods report separate concentrations for discrete aliphatic and aromatic fractions. The available methods are GC-based and are thus sensitive to a broad range of hydrocarbons. Identification and quantification of aliphatic

and aromatic fractions allows one to identify products and evaluate the extent of product weathering. These fraction data also can be used in risk assessment.

Metals Content

Metals content in a feedstock or related product (especially in the case of biomass feedstocks and the related products) can provide valuable information in identifying the source of a spill as well as the potential for problems during upgrading these materials. Oil spills.

Feedstock and product assays should always include the presence and content of various metals due to the detrimental effects of metals on catalysts used in cracking and desulfurization processes.

Molecular Weight

The molecular weight (formula weight) of a compound is the sum of the atomic weights of all the atoms in a molecule and can be determined by a variety of methods. Fuels (from whatever the source) are complex mixtures of (at least) several hundred constituents requires qualification of the molecular weight as either (i) number average molecular weight or (ii) weight average molecular weight.

The *number average molecular weight* is the ordinary arithmetic mean or average of the molecular weights of the individual constituents. It is determined by measuring the molecular weight of n molecules, summing the weights, and dividing by n . On the other hand, the *weight average molecular weight* is a way of describing the molecular weight of a complex mixture even if the molecular constituents are not of the same type and exist in different sizes. Molecular weight is often used in refineries to provide mass-average or number-average measurements. Consequently, a number of methods are available to measure the molecular weight of feedstocks and products.

If the molecular weight determination involves the use of a solvent, it is recommended that to negate concentration effects and temperature effects, the molecular weight determination be carried out at three different concentrations at three different temperatures. The data for each temperature are then extrapolated to zero concentration, and the zero concentration data at each temperature are then extrapolated to room temperature.

Furthermore, each method of molecular weight determination has proponents and opponents because of assumptions made in the use of the method or because of the mere complexity of the sample and the nature of the inter- and intra-molecular interactions. Also, indirect methods have been proposed for the estimation of molecular weight by correlation with other, more readily measured physical properties. They are satisfactory when dealing with the conventional type of crude oils or their fractions and products when approximate values are desired.

Pour Point

The pour point of a feedstock or a related product is the lowest temperature at which the feedstock (or product) will flow, under standard test conditions. The failure to flow at the pour point is usually attributed to the separation of waxes from the feedstock or the product but can also be due to the effect of viscosity in the case of very viscous materials. Also, the pour point may be influenced by the thermal history of the sample, that is, the degree and duration of heating and cooling to which the sample has been exposed.

Sulfur Content

The sulfur content of a material is important for a number of reasons. Downstream processes such as catalytic cracking and refining will be adversely affected by a high sulfur contents. If high sulfur oils are burned, they produce high levels of sulfur dioxide which can lead to acid deposition (acid rain).

The total sulfur content of material can be determined by numerous standard techniques, and the methods are applicable to both volatile and non-volatile feedstocks and products.

Surface Tension and Interfacial Tension

Interfacial tension is the force of attraction between the molecules at the interface of two fluids. At the air/liquid interface, this force is often referred to as surface tension. The surface tension of a material, together with the viscosity, affects the rate at which a spilled material will spread. Air/oil and oil/water interfacial tensions can be used to calculate a spreading coefficient which gives an indication of the tendency for the oil to spread and which is defined as:

$$\text{Spreading coefficient} = S_{\text{WA}} - S_{\text{OA}} - S_{\text{WO}}$$

S_{WA} is water/air interfacial tension, S_{OA} is oil/air interfacial tension, and S_{WO} is water/oil interfacial tension. Unlike density and viscosity, which show systematic variations with temperature and degree of evaporation, interfacial tensions of many biomass-derived feedstocks and products may not show such correlations.

Total Acid Number

No matter what the source of the fuel, but especially when the fuel is produced directly from biomass, there is a risk that the fuel may have acidic constituents which can have an adverse effect on the performance of the fuel and cause corrosion in the system. The acidic properties of any fuel can be determined by a test method that determines such constituents. The test data are presented as the total acid number. The total acid number (TAN) represents a composite of acids present in the feedstock or the fuel and is often also expressed as the neutralization number.

In the test method, the sample normally dissolved in a solvent (such as toluene/is-propyl alcohol/water) is titrated with potassium hydroxide and the results are expressed as milligrams of potassium hydroxide per gram of sample (mg KOH/gm). Feedstocks and fuels having high acid numbers have a high potential to cause corrosion problems in equipment, especially in the atmospheric and vacuum distillation units where there may also be water present and the hot material comes into contact with hot metal surfaces. Crude oil typically has a total acid number (TAN value) on the order of 0.05 to 6.0 mg KOH/gm of sample.

The impact of corrosive, high TAN, feedstocks and fuels can be overcome by blending higher and lower TAN feedstocks or fuels, installing or retrofitting equipment with anticorrosive materials, or by developing low-temperature catalytic de-acidification processes using metal catalysts such as copper.

Viscosity

Viscosity is a measure of the resistance of a fluid to flow – the lower the viscosity of a fluid, the more easily it flows. Like density, viscosity is affected by temperature. As temperature decreases, viscosity increases. Viscosity is an important property of feedstocks and products because it affects (i) the rate at which a spilled material will spread, (ii) the degree to which the spilled material will penetrate shoreline substrates, and (iii) the selection of mechanical spill countermeasures equipment.

Viscosity measurements may be absolute or relative – the latter is sometimes called apparent viscosity. Absolute viscosity is measured by a standard method, with the results traceable to fundamental units. The absolute viscosity is distinguished from the relative viscosity that is made with instruments that measure viscous drag in a fluid, without known and/or uniform applied shear rates. An important benefit of absolute viscometry is that the test results are independent of the particular type or make of viscometer used and the absolute viscosity data can be compared easily between laboratories worldwide.

Water Content

Some of the feedstocks and products produced from alternative energy sources may contain substantial amounts of water. Therefore, for materials with significant water contents, (>5% w/w), many of the properties measured will not represent the properties of the *dry* material.

Water content has not been conclusively identified as a direct governing environmental factor in the biodegradation of spilled materials, but an indirect effect of water content is that it influences the effective gas diffusion coefficient in soils. The rate of production of carbon dioxide is a means of expressing the mineralization rate of spilled products.

See also: Acid Rain, Fractional Composition.

Product Analysis – Chromatographic Methods

Product analyses are conducted to determine the amounts of the compound classes present in many feedstocks and products. This type of measurement is sometimes used to identify fuel type or to track plumes. It may be particularly useful for higher-boiling products. Group type test methods include multidimensional gas chromatography

(not often used for environmental samples), high performance liquid chromatography (HPLC), and thin layer chromatography.

Common constituent measurement techniques include gas chromatography with second column confirmation, gas chromatography with multiple selective detectors, and gas chromatography with mass spectrometry detection (GC/MS).

Gas Chromatography

Gas chromatography (GC), which is based on the principle of a stationary phase and a mobile phase, remains a primary technique for determining constituents distribution in many feedstocks and products through the identification of individual constituents. Although a measure of purity by gas chromatography is often sufficient for many purposes, it is not always sufficient for measuring absolute purity – not all possible impurities will pass through the chromatographic column, and not all those that do will be measured by the detector. Absolute purity is best measured by distillation range or freeze or solidification points. Despite this disadvantage, the technique is still widely used and is the basis of many current standard test methods for the determination and measurement of the constituents in many process feedstocks and products.

Gas-liquid chromatography (GLC) is a method for separating the volatile components of various mixtures. It is, in fact, a highly efficient fractionating technique, and it is ideally suited to the quantitative analysis of mixtures when the possible components are known and the interest lies only in determining the amounts of each present. In this type of application, gas chromatography has taken over much of the work previously done by the other techniques; it is now the preferred technique for the analysis of hydrocarbon gases, and gas chromatographic in-line monitors are having increasing application in refinery plant control. Gas-liquid chromatography is also used extensively for individual component identification, as well as percentage composition, in the gasoline boiling range.

The mobile phase is the carrier gas, and the gas selected has a bearing on the resolution. Nitrogen has poor resolution ability, while helium and hydrogen are better choices with hydrogen being the best carrier gas for resolution. However, hydrogen is reactive and may not be compatible with all sets of target analytes. There is an optimum flow rate for each carrier gas to achieve maximum resolution. As the temperature of the oven increases, the flow rate of the gas changes due to thermal expansion of the gas. Most modern gas chromatographs are equipped with constant flow devices that change the gas valve settings as the temperature in the oven changes, so changing flow rates are no longer a concern. Once the flow is optimized at one temperature, it is optimized for all temperatures.

Gas Chromatography-Mass Spectrometry

A gas chromatography-mass spectrometry system is used to measure concentrations of the target volatile and semi-volatile of the sample. The advantage of the technique is the high selectivity, or the ability to confirm compound identity through retention time and a unique spectral pattern. The method is used for identification and quantification of the constituents of feedstocks and products.

To reduce the possibility of false positives, the intensities of one-to-three selected ions are compared to the intensity of a unique target ion of the same spectrum. The sample ratios are compared to the ratios of a standard. If the sample ratios fall within a certain range of the standard, and the retention time matches the standard within specifications, the analyte is considered present. Quantification is performed by integrating the response of the target ion only.

Mass spectrometers are among the most selective detectors, but they are still susceptible to interferences. Isomers have identical spectra, while many other compounds have similar mass spectra. Feedstocks and products may contain thousands of major components that are not resolved by the gas chromatograph. As a result, multiple compounds are simultaneously entering the mass spectrometer. Different compounds may share many of the same ions, confusing the identification process. The probability of misidentification is high in complex mixtures.

High-Performance Liquid Chromatography

A high-performance liquid chromatography system can be used to measure concentrations of target semi-volatile and non-volatile constituents of mixtures. The system only requires that the sample be dissolved in a solvent compatible with those used in the separation. The detector most often used in environmental analysis is the fluorescence

detector. These detectors are particularly sensitive to aromatic molecules, especially polynuclear aromatic hydrocarbons. An ultraviolet detector may be used to measure compounds that do not fluoresce.

Interfering compounds will vary considerably from source to source, and samples may require a variety of clean-up steps to reach the required method detection limits. The emission wavelengths used (EPA 8310) are not optimal for the sensitivity of the small ring compounds. With a modern electronically-controlled monochromator, wavelength programs can be used which tune excitation and emission wavelengths to maximize sensitivity and/or selectivity for a specific analyte in its retention time window.

Thin Layer Chromatography

In the environmental field, thin layer chromatography (TLC) is best used for screening analyses and characterization of semi-volatile and non-volatile materials. The precision and accuracy of the technique is inferior to other methods, but when speed and simplicity are desired, thin layer chromatography may be a suitable alternative. For characterizations of high-boiling constituents, the method has the advantage of separating compounds that are too high boiling to pass through a gas chromatograph. While thin layer chromatography does not have the resolving power of a gas chromatograph, it is able to separate different classes of compounds. Thin layer chromatography analysis is fairly simple and, since the method does not give highly accurate or precise results, there is no need to perform the highest-quality extractions.

The method is considered to be a qualitative and useful tool for rapid sample screening. Limitations of the method center on its moderate reproducibility, detection limits, and resolving capabilities. Variability between operators can be as high as 30%. It is often not possible to distinguish between similar products, and, as with all chemical analyses, quality assurance tests should be run to verify the accuracy and precision of the method.

Product Analysis – Spectroscopic Methods

The chemical composition of a feedstock has always been considered to be a valuable indicator of refining behavior. Whether or not it is the ultimate indicator of refining behavior remains to be seen and is audience dependent! More than likely, chemical composition studies truly complement physical property and physical behavior studies and the true picture is a combination of all of these studies.

However, the chemical composition of a feedstock is represented in terms of compound types and/or in terms of generic compound classes, thus allowing the analytical chemist, the process chemist, the process engineer, and the refiner to determine the nature of the reactions. Hence, chemical composition can play a large part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed. However, proper interpretation of the data resulting from the composition studies requires an understanding of chemical structures, their significance, and an open mind!

The physical and chemical characteristics of feedstocks and the yields and properties of products or factions prepared from them vary considerably and are dependent on the concentration of the various types of hydrocarbons and minor constituents present. Some types of biomass-related feedstocks have economic advantages as sources of fuels with highly restrictive characteristics because they require less specialized processing than that needed for production of the same products from many types of feedstocks. Others may contain unusually low concentrations of components that are desirable fuel or lubricant constituents, and the production of these products from such crude oils may not be economically feasible.

Spectroscopic studies have played an important role in the evaluation of feedstocks and their respective products for the last six decades, and many of the methods are now used as standard methods of analysis for refinery feedstocks and products.

Infrared Spectroscopy

Infrared spectroscopy is a well-established method that was developed for comparative, semi-quantitative analysis leading to the present quantitative analysis. Infrared spectra are displayed either as percent transmittance or as absorptivity versus frequency (cm^{-1}). Transmittance, T , defined as the ratio of transmitted light over incident light, or percent transmittance, usually shows more detail over the entire range and is generally the preferred display.

Absorbance, A , on the other hand, is proportional to the concentration and is, therefore, used for quantitative measurements.

In combination with nuclear magnetic resonance spectroscopy, infrared spectroscopy is a simple procedure and is one of several techniques that can provide quick information about the distribution of several structural and functional groups. However, in the context of high-molecular-weight constituents, conventional infrared spectroscopy yields information about the functional features of various feedstock and product constituents. For example, infrared spectroscopy will aid in the identification of imino functions ($=N-H$) and hydroxyl ($-O-H$) functions, as well as the nature of the various carbonyl ($-C=O$) functions.

With the more recent progress of *Fourier transform infrared (FTIR) spectroscopy*, quantitative estimates of the various functional groups can also be made. This is particularly important for application to the higher-molecular-weight solid constituents of feedstock and products and for group-type analysis. Also, the newer diffuse reflectance infrared (DRIR) techniques seem to give equally good spectra as obtained in conventional ways from solutions in cells or from potassium bromide (KBr) pellets. Another synonym for this technique is DRIFT (for diffuse reflectance infrared Fourier transform).

Band assignments for infrared spectra were established several decades ago. Resolution enhancement by Fourier self-deconvolution (band narrowing) led to the recognition and distinction of bands that could previously not be separated. Examples of such new assignments are methyl (CH_3) groups next to aromatic rings ($2,948\text{ cm}^{-1}$) and next to alkyl groups ($2,960\text{ cm}^{-1}$), methylene (CH_2) groups (together with some methyl groups) next to aromatic rings ($2,916\text{ cm}^{-1}$) and in aliphatic chains ($2,926\text{ cm}^{-1}$), methylene groups next to an alkoxy function ($2,928\text{ cm}^{-1}$) and next to a carbonyl group ($2,933\text{ cm}^{-1}$); and methane (CH) groups in unspecified environments ($2,905\text{ cm}^{-1}$ and $1,897\text{ cm}^{-1}$). The rocking vibration band of methylene groups in straight aliphatic chains varies slightly with their length. For n -pentyl groups, it is located at 726 cm^{-1} , and with longer chains, it shifts to lower frequencies until it stabilizes at 720 cm^{-1} for chains with more than nine carbon atoms.

Mass Spectrometry

Mass spectrometry furnishes the molecular weight and chemical formula of compounds and their relative amounts in a mixture and offers a non-destructive examination of the sample. The technique can also provide important information about their molecular structure. The earliest and most common type of mass spectrometry, electron impact mass spectrometry (EI-MS), gives a fragmentation pattern displaying both parent ion peaks and fragment ion peaks, characteristic of each molecular type.

Fragmentation is frequently employed to differentiate between isomers of pure compounds and of molecules in fairly simple mixtures. However, it is usually avoided with such complex samples as high-molecular-weight materials, which are composed of such a multitude of closely related compounds that their fragmentation patterns are non-distinctive and cannot be readily interpreted.

Mass spectrometry can play a key role in the identification of the constituents of feedstocks and products either in the laboratory or online. The principal advantages of mass spectrometric methods are (i) high reproducibility of quantitative analyses, (ii) the potential for obtaining detailed data on the individual components and/or carbon number homologues in complex mixtures, and (iii) a minimal sample size is required for analysis. The ability of mass spectrometry to identify individual components in complex mixtures is unmatched by any modern analytical technique. Perhaps the exception is gas chromatography.

However, there are disadvantages arising from the use of mass spectrometry and these are: (1) the limitation of the method to organic materials that are volatile and stable at temperatures up to 300°C (570°F); and (2) the difficulty of separating isomers for absolute identification. The sample is usually destroyed, but this is seldom a disadvantage. Nevertheless, in spite of these limitations, mass spectrometry does furnish useful information about the composition of feedstocks and products even if this information is not as exhaustive as might be required. There are structural similarities that might hinder identification of individual components. Consequently, identification by type or by homologue will be more meaningful since similar structural types may be presumed to behave similarly in processing situations. Knowledge of the individual isomeric distribution may add only a little to an understanding of the relationships between composition and processing parameters.

High-voltage electron impact mass spectrometry (HVEI-MS or EI-MS) can cause repeated fragmentation of daughter ions. Considering the repeated fragmentation of even the simplest hydrocarbons and the fact that the

higher-molecular-weight fractions of feedstocks and products may contain such a broad range of molecular weight species, the patterns obtained from these types of materials are so complex as to almost defy interpretation. Thus, non-fragmenting mass spectrometric methods are preferred.

For high-molecular-weight feedstocks and products, the use of non-fragmenting mass spectrometry (NF-MS) methods is now preferred. These methods, also called *soft ionization* methods, produce predominantly parent ion (molecular ion) peaks and, thus, much simpler spectra than methods producing fragments. By rendering the molecular weight of each compound in a sample, and reasonably well its abundance, non-fragmenting mass spectrometry also can be used to determine the molecular weight distribution, i.e., the molar mass profile of a sample.

Indeed, the great advantage of *non-fragmenting mass spectrometry* is the relative simplicity of the spectra. A disadvantage is the relatively low signal intensity of the ions. With *low-voltage electron impact ionization*, the number of parent ions formed increases rapidly as the ionizing voltage increases above the ionizing potential of the molecules in the sample. Thus, a higher voltage gives a more intense signal (up to about 20-40 eV, depending on compound type). However, the higher ionizing voltage transfers more energy to the sample molecules and causes fragmentation to increase. The surplus energy transferred to the molecule in excess of the ionizing potential is equilibrated and dissipated in various ways, for example, by increasing the internal energy of the molecule or by breaking atomic bonds.

Among the most important non-fragmenting mass spectrometric techniques are field ionization mass spectrometry (FIMS), field desorption mass spectrometry (FDMS), chemical ionization mass spectrometry (CIMS), and low-voltage (10-20 eV) electron impact mass spectrometry (LVEI-MS). A particularly powerful version of electron impact mass spectrometry is high-resolution electron impact mass spectrometry (HR-LEVI-MS or LVRH-MS). All of these are designed to generate *cold* ions of such low excess energy that they do not undergo fragmentation to any great extent, in contrast to the *hot* ions generated by conventional electron impact ionization (70 to 100 eV). With such ionization methods, a compromise must be found between low fragmentation and sufficiently high sensitivity. Unfortunately, samples rich in aliphatic hydrocarbons are hard to keep completely from fragmenting, but most other compound types, especially aromatic compounds, yield clean parent ion spectra.

Field ionization mass spectrometry shows extremely low fragmentation because the ionization process imparts little excess energy to the formed ion. This is crucial when ionizing saturates. Both low-voltage electron impact (LVEI) and chemical ionization (CI) transfer more excess energy than field ionization mass spectrometry, leading to higher levels of fragmentation with saturates. As long as the analyte is volatile, the field ionization mass spectrometry experiment is not sample limited. That is, additional sample can be vaporized as needed to obtain the required signal-to-noise ratio. Field desorption mass spectrometry (FDMS) can be considered a special form of electron impact mass spectrometry (EIMS) where the sample material is placed on the ionizing surface of the probe before insertion into the sample chamber of the mass spectrometer. It is, however, sample limited and subject to experimental artifacts not normally present in electron impact mass spectrometry.

In the electron impact mass spectrometry technique, the emitting surface is a cathode consisting of an array of sharp tips on a support such as a wire, a grid, or a razor blade. This surface is located close to the anode. The combination of an extremely small radius of curvature of the tips, the short distance, and the high electric field creates a high field gradient. The sample is introduced to this field gradient by evaporation and diffusion from a heated surface nearby.

Field desorption mass spectrometry is a special form of field ionization mass spectrometry. The cathode is the same, but here it is coated with the sample before it is placed in the mass spectrometer source. This eliminates the need to evaporate the sample and any losses on transport to the cathode. Instead, the ions are desorbed directly from the solid sample. The emitter is heated to the point where the sample melts and can be drawn by the surface tension to the tip where the molecules are converted to ions. As the ions are ejected from the surface into the mass spectrometer, more sample molecules can replace them at the tip. In this way, labile molecules can be handled without significant fragmentation, and even conventionally nonvolatile samples can be run. Thus, the method is especially suitable for the high-molecular-weight fractions of non-volatile materials. Because of the low thermal energy to which the sample molecules are exposed, the total excess energy in this process is minimal. Thus, field desorption mass spectrometry is an even milder method than field ionization mass spectrometry and produces less fragmentation.

Chemical ionization mass spectrometry (CI-MS), another *soft* method, has been used only occasionally for non-volatile with mixed success. In the method, a relatively high-pressure reagent gas (e.g., methane, *n*-butane, *iso*-butane) is ionized and allowed to contact the sample. At such pressures, the reagent ions undergo many collisions

that help them lose excess energy left after ionization. The ions also exchange charges during collision with one another and with the sample molecules. The latter is the desired reaction, and the method works best when the sample molecules retain the charge better than the reagent molecules.

Fast atom bombardment mass spectrometry (FAB-MS) is a method in which the sample is dissolved in a high-boiling polar liquid matrix (such as glycerol or triethanolamine) and spread on a plate. Rare gas molecules (e.g., xenon or argon) are ionized, accelerated, focused at the sample, and stripped of their charge before they hit their target. The impact of uncharged atoms sputters small amounts of the matrix and sample off the sample plate. The liquid matrix evaporates, liberating charged sample ions, which are now propelled by the accelerating voltage into the mass spectrometer.

Nuclear Magnetic Resonance

Nuclear magnetic resonance has frequently been employed for general studies of hydrogen types in feedstocks and products. The technique has recently been adapted to measure the hydrogen content of fuels and, in fact, *proton magnetic resonance* (PMR) studies (along with infrared spectroscopic studies) were, perhaps, the first studies of the modern era that allowed structural inferences to be made about the polynuclear aromatic systems that occur in the high-molecular-weight constituents of feedstocks and products.

The technique presents a direct measure of the aromatic and aliphatic carbon as well as hydrogen distribution. Beyond these results, both carbon and hydrogen in various structural groupings in a molecule can be determined. Thus, proton (^1H) and carbon-13 (^{13}C) nuclei are the most common ones used in nuclear magnetic resonance spectroscopy; nitrogen (^{15}N and ^{14}N) and sulfur (^{33}S) have been employed on occasion for special applications.

Only a small amount (<10 mg) of the sample is required, dissolved in a solvent such as deuterio-chloroform, contained in a glass tube of 5 mm diameter and placed in a highly homogeneous magnetic field where it is surrounded by one or more coils. The coils serve to subject the sample to a weak radio-frequency (RF) field. The hydrogen nuclei of the sample can be visualized as magnets, and when the radio frequency is equal to the processing frequency, resonance occurs between the two, and the spin resonance is detected by a receiver coil. The position of a sample resonance with that of tetramethylsilane (TMS) as a reference difference is reported as *chemical shift*, δ , which is a dimensional number that is expressed in terms of parts per million (ppm) difference from the reference (TMS).

Carbon-13 magnetic resonance (CMR) can play a useful role. Since carbon magnetic resonance deals with analyzing the carbon distribution types, the obvious structural parameter to be determined is the aromaticity, f_a . A direct determination from the various carbon-type environments is one of the better methods for the determination of aromaticity. Thus, through a combination of proton and carbon magnetic resonance techniques, refinements can be made on the structural parameters and, for the solid state high resolution CMR technique, additional structural parameters can be obtained.

Thus, proton and carbon-13 magnetic resonance spectroscopic techniques offer the potential information about the molecular types in the non-volatile fractions of feedstocks and products. The techniques have, by the application of the estimation of peak areas and further application of mathematical methods, been used to obtain information about *structural parameters* that are then converted to *average structures*.

Ultraviolet Spectroscopy

The ultraviolet-visible (UV-Vis) spectrum, although not as specific for chemical group types as is infrared spectroscopy and nuclear magnetic resonance spectroscopy, can distinguish between aromatic compounds with different ring numbers and configurations. The patterns are not distinct enough to recognize or distinguish these compounds in complex mixtures, but they can be useful for their identification in narrow fractions.

Ultraviolet-visible spectroscopy can be employed as a detector for the fractionation of various samples, for example, for the chromatographic separation and/or identification of aromatics by ring number, especially in combination with a technique such as liquid chromatography. Thus, ultraviolet-visible spectroscopy lends itself to studies of refining processes as an online detector.

X-Ray Diffraction

X-ray diffraction had been used for the determination of the fraction of aromatic carbon (f_a) in feedstocks and, in some cases, products. This ratio can also be conveniently and precisely obtained by carbon-13 nuclear magnetic

resonance spectroscopy as well as by infrared spectroscopy. The determination of the fraction of carbon that is aromatic may be in error since X-ray diffraction data can be very misleading, especially when the data are used to translate geometric data – measurements of (aromatic) sheet diameter – into structural information. On the one hand, not all aromatic atoms contribute to the stack diameter seen by x-ray diffraction whereas, on the other hand, non-aromatic atoms such as hydroaromatic carbons and other substituents on aromatic rings may contribute to the diffraction pattern. Thus, the interpretation of these measurements is quite arbitrary.

Extended x-ray absorption fine structure (EXAFS) and *x-ray absorption near-edge structure* (XANES) spectroscopy are tools for the investigation of the immediate chemical environment of x-ray absorbing elements such as metals and sulfur. X-ray absorption near-edge structure and x-ray photoelectron spectroscopy (XPS) have been applied to the determination of sulfur compounds in samples.

Product Blending

The modern crude oil refinery consists of a complex mix of high technology processes which efficiently convert the wide array of crude oils into the hundreds of specification products that are in daily use. Each refinery has its own unique processing configuration as a result of the logistics and associated economics related to its specific crude oils and products markets. The refiner must continuously optimize the mix of product volumes, and this is accomplished through executing decisions regarding parameters as varied as crude oil feedstock selection, adjustments in product cut-points, and reactor severities in individual processes. Additional options include changing the dispositions of intermediate product streams to alternative processing units, or alternative finished product blends.

In fact, many refinery products are typically the result of blending several component streams or blending stocks. In most cases, product blending is accomplished by controlling the volumes of blend stocks from individual component storage tanks that are mixed in the finished product storage tank. Samples of the finished blend are then analyzed by laboratory testing for all product specifications prior to shipping. Alternatively, in-line blending refers to pipeline shipments in which the finished product is actually blended directly into the product pipeline (as opposed to a standing product storage tank).

The most commonly recognized blending operations occur in the gasoline production section of the refinery. The various gasoline streams are so that specifications (dependent upon geographic location, environmental regulations, and weather patterns) can be met.

Gasoline blending involves combining of the components that make up motor gasoline. The components include the various hydrocarbon streams produced by distillation, cracking, reforming, and polymerization, tetraethyl lead, and identifying color dye, as well as other special-purpose components, such as solvent oil and anti-icing compounds. The physical process of blending the components is simple, but determination of how much of each component to include in a blend is much more difficult. The physical operation is carried out by simultaneously pumping all the components of a gasoline blend into a pipeline that leads to the gasoline storage, but the pumps must be set to automatically deliver the proper proportion of each component. Baffles in the pipeline are often used to mix the components as they travel to the storage tank.

Selection of the components and their proportions in a blend is the most complex problem in a refinery. Many different hydrocarbon streams may need to be blended to produce quality gasoline. Each property of each stream is a variable, and the effect on the product gasoline is considerable. For example, the low octane number of straight-run naphtha limits its use as a gasoline component, although its other properties may make it desirable. The problem is further complicated by changes in the properties of the component streams due to processing changes. For example, an increase in cracking temperature produces a smaller volume of higher octane cracked naphtha, but before this cracked naphtha can be included in a blend, adjustments must be made in the proportions of the other hydrocarbon components. Similarly, the introduction of new processes and changes in the specifications of the finished gasoline dictate reevaluation of the components that make up the gasoline.

Gasoline blending is not the only blending operation; other product blending operations are also in operation in a refinery. The applicable specifications vary by product but typically include properties pertinent to the behavior of the product in use. Many product specifications do not blend linearly by component volumes. In these

circumstances, the finished blend properties are predicted using experience-based algorithms for the applicable blending components.

See also: Refining.

Product Improvement

From a chemical standpoint, fuels produced from alternate feedstocks are complex mixtures of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds.

For the purposes of terminology, it is preferable to subdivide crude oil and related biomass liquids materials into three major classes which are: (i) materials that are of natural origin, (ii) materials that are manufactured, and (iii) materials that are integral fractions derived from the natural or manufactured products.

The materials included in categories 1 and 2 are relevant here because of their participation in product streams. Straight-run constituents of crude oil (i.e., constituents distilled without change from crude oil) are used in products. Manufactured materials are produced by a variety of processes and are also used in product streams. Category 3 materials are usually those materials that are isolated from crude oil or from a product by the use of a variety of techniques.

The production of liquid product streams by distillation or by cracking processes are only the first of a series of steps that lead to the production of marketable liquid products. Several other unit processes are involved in the production of a final product. Such processes may be generally termed *secondary processes* or *product improvement processes* since they are not used directly on the crude oil but are used on primary product streams that have been produced from the crude oil.

In addition, the term product improvement includes processes such as reforming processes in which the molecular structure of the feedstock is reorganized. An example is the conversion (*reforming*, *molecular rearrangement*) of *n*-hexane to cyclohexane or cyclohexane to benzene. These processes *reform* or *rearrange* one particular molecular type to another, thereby changing the properties of the product relative to the feedstock. Such processes are conducive to expansion of the utility of crude oil products and to sales.

See also: Refining.

Production of Organic Matter in Aqueous Environments

Photosynthesis by phytoplankton, especially blue-green algae (Cyanophyceae), diatoms, dinoflagellates, and in warmer waters by phyto bacteria, is ultimately responsible for producing nearly all of the organic matter in the oceans.

A precise quantitative relationship between the fossil record and organic productivity is not available; many productive species have no hard body parts that are easily preserved. Hence, the productivity may not be reflected in the surviving fossils. Nevertheless, as pointed out by Moore, the fossil record indicates significant differences between production in marine and lacustrine environments.

Photosynthetic productivity is mainly controlled by light, temperature, and nutrient availability. Light seems not to be the controlling factor, except in deep water, Polar Regions, or turbid coastal regions. The availability of carbon dioxide, which is essential for photosynthesis, is not limiting in the *eutrophic zone* (the top 200 meters, or so, where productivity is highest). Rather, nutrient availability – often nitrogen (as ammonium or nitrate) in marine or phosphate in lacustrine, environments seems to be the most common limit on productivity. The availability of vitamins, especially of vitamin B12, and other trace organics is important, and seems to be a limiting factor in some areas. Productivity in lakes follows the same general pattern as in oceans, but deposition in the confines of a lake is much more subject to local climatic variations and periodic changes in clastic input (e.g., volcanic ash) than is marine deposition.

See also: Photosynthesis.

Product Treating

Fractions or streams produced from alternate (non-fossil fuel sources) often contain variable amounts of impurities that must be removed. Processes that remove these undesirable components are known as treating processes, and these processes are used not only to finish products for the market but also to prepare feedstocks for other processes (*catalytic polymerization* and *reforming*) in which catalysts would be harmed by impurities.

The undesirable components in a crude oil fraction are referred to as impurities, but they are almost invariably either the normal constituents of crude oil or they are derivatives of the constituents of crude oil. The most common impurities are sulfur compounds that are derived from the sulfur compounds that occur in crude oil, such as sulfides (R^1SR^2) and the foul-smelling mercaptan derivatives (RSH), also called thiols. Oxygen compounds in the form of carboxylic acid derivatives (RCO_2H) and phenol derivatives ($ArOH$, where Ar is an aromatic group) may also be present. Nitrogen-containing compounds derived from those that occur in crude oil are also present.

Sometimes, olefins ($R^1CH=CHR^2$, R^1 and R^2 may or may not be similar hydrocarbon groups) must be eliminated from a feedstock or aromatics removed from a solvent, and these olefins and aromatics are considered impurities. Similarly, polymerized material, asphaltic material, or resins may be impurities, depending on whether their presence in a finished product is harmful.

During processing, much of the sulfur originally in the crude oil is converted to hydrogen sulfide (H_2S) and mercaptans ($R-SH$). Some sulfur may be retained in any coke that is formed. Processes that are primarily concerned with the removal of hydrogen sulfide and mercaptans are known as *sweetening* processes. Crude oil fractions containing mercaptans are readily recognized by their odor and are called *sour*. Fractions that are free of obnoxious sulfur compounds, either naturally or because of treatment, are called *sweet*, but a sweet fraction may contain sulfur compounds (e.g., sulfide R^1SR^2 or disulfide R^1SSR^2) that have no odor. The more severe desulfurization of crude oil fractions is not usually classed as a treating process, but recognition has been given to processes such as hydrotreating processes and hydrocracking processes that contribute to product improvement.

The need to remove sulfur (desulfurization) from various feedstocks is of significant importance. Thus, desulfurization is a major refinery issue and is worthy of mention here. Indeed, considerable importance has been attached to the lowering of the sulfur level in distillates and residual stocks. For example, the stability of sulfur compounds is greatly reduced when they are heated in the presence of adsorptive catalysts, and this is employed in a number of desulfurization processes. The non-cyclic sulfur compounds (mercaptans, RSH , sulfides, RSR , and disulfides, $RSSR$) in straight-run distillates (such as naphtha) are readily converted into hydrogen sulfide and olefins by contacting the vapors with clays, aluminum oxide, or alumina-silica ($Al_2O_3-SiO_2$) cracking catalysts. These processes generally operate at approximately 345 to 425°C (650 to 800°F) and at a pressure of approximately 50 psi.

When hydrogen is added and a dehydrogenation catalyst, such as cobalt sulfide and molybdenum sulfide on alumina, is employed, extensive desulfurization or denitrogenation of a wider spectrum of heteroatomic compounds is achieved. Even the refractory cyclic nitrogen and sulfur compounds are decomposed, and the heteroatom is released as its hydrogen analog (e.g., H_2S or NH_3).

Treatment processes for the removal of sulfur-containing and nitrogen-containing compounds are much less severe than the desulfurization and denitrogenation processes. In fact, it is generally recognized that the removal or conversion of sulfur and nitrogen compounds in distillates by treatment processes is usually limited to mercaptans and the lower-molecular-weight sulfur compounds. When there is more than a trace amount ($>0.1\%$) of heteroatoms present, it is often more convenient and economical to resort to such methods as those thermal processes (e.g., hydroprocesses) that bring about a decrease in all types of heteroatomic compounds.

Choices of a treatment method depend on the amount and type of impurities in the fractions to be treated and the extent to which the process removes the impurities. Naturally occurring sweet kerosene, for example, may require only a simple treatment with alkali (*lye*) to remove hydrogen sulfide. If mercaptans are also present in the raw kerosene, a doctor treatment in addition to *lye treatment* is required, but poor-quality raw kerosene may require, in addition to these treatments, treatment with sulfuric acid and Fuller's Earth. The lowest quality raw kerosene requires treatment with strong sulfuric acid, neutralization with lye, and redistillation. Since different fractions have the same impurities, the same treatment process may be used for several different products.

There is a choice of several different treatment processes, but the primary purpose of the majority is the elimination of unwanted sulfur compounds. Some processes are limited to the conversion of certain sulfur compounds, as well as olefins, asphaltic materials, oxygen compounds, and nitrogen compounds. The various processes eliminate impurities by chemical reagents, by catalysts, and by adsorption on clays or similar materials. Some chemical treatment processes directly remove sour sulfur compounds and hence tend to supplant the older processes that sweeten by conversion of sulfur compounds. Caustic soda (*lye*) solutions have long been used to remove hydrogen sulfide and some of the lower-boiling mercaptan derivatives. Caustic soda, however, does not remove the higher-boiling mercaptans. By combining caustic soda solution with various solubility promoters (methyl alcohol, cresols, naphthenic acids, and alkyl phenols), up to 99% of all mercaptans as well as oxygen and nitrogen compounds can be dissolved from crude oil fractions.

Sulfuric acid (H_2SO_4) treatment has the longest history of any crude oil-treating method. Sulfuric acid was the preferred treating material for all crude oil fractions from naphtha to lubricating oil for a century and is still widely used. Modern use of sulfuric acid is only a fraction of its former use. Nevertheless, the removal or conversion of mercaptans can be effected by sulfuric acid or by anhydrous aluminum chloride (AlCl_3), but the chemistry of the sulfuric acid desulfurization is not fully understood. Sulfides and disulfides are removed by addition reactions with aluminum chloride or by solution with sulfuric acid. Cyclic sulfides, such as tetramethylene and pentamethylene sulfide as well as sulfones $[\text{R}-\text{S}(=\text{O})-\text{R}]$ and sulfoxides $[\text{R}-\text{S}(\text{O})_2-\text{R}]$, are also removed by solution in the acid.

A number of commonly used treatment processes (doctor treatment, copper chloride treatment, and sodium hypochlorite treatment) convert mercaptans into odorless disulfides, which remain dissolved in the crude oil fraction. If no harm will result from a small amount of disulfides, they may be left in finished products, such as kerosene or stove oil. When sulfur compounds cannot be tolerated, as in solvent naphtha, disulfides are removed in a bottom fraction obtained by redistilling the sweetened naphtha.

Hypochlorite derivatives, for example sodium hypochlorite (NaOCl , bleaching powder), oxidize mercaptans (RSH) to disulfides (RSSR) and alkyl sulfides (thioethers) (RSR) are oxidized to sulfoxides $[\text{RS}(\text{O})_2\text{R}]$. The lower-molecular-weight products may be water-soluble.

Mercaptan derivatives (e.g., $\text{RCH}_2\text{CH}_2\text{SH}$) may also be removed from refinery products in a process in which they are converted to hydrogen sulfide (H_2S) and the corresponding olefin ($\text{RCH}=\text{CH}_2$), either by heat alone or, more easily, in the presence of catalysts such as bauxite (crude alumina, Al_2O_3). However, thioethers may be produced if the catalyst contains zinc sulfide (ZnS) and/or cadmium sulfide (CdS).

Propane

Commercial Propane consists predominantly of propane and/or propylene, while Commercial Butane is mainly composed of butanes and/or butylenes. Both must be free from harmful amounts of toxic or nauseating substances and free from mechanically entrained water. In the case of Commercial Propane, water content may be further limited by specific tests.

Commercial propane-butane mixtures are produced to meet particular requirements and find application as fuels in areas and at times where low ambient temperatures are less frequently encountered. Typical specifications contain clauses covering volatility, vapor pressure, specific gravity, hydrocarbon composition, sulfur and its compounds, corrosion of copper, residues, and water content.

Special Duty Propane is intended for use in spark-ignition engines. In Europe, this demand is often met by the commercial grades described above, but in USA, a tightly controlled C_3 mixture is specified. In addition to the usual clauses, the specification includes a minimum motor octane number to ensure satisfactory antiknock performance. Propylene has a significantly lower octane number than propane, so there is a limit to the amount of this component that can be tolerated in the mixture.

Volatility, vapor pressure, and relative density

The vaporization and combustion characteristics of commercial liquefied gas products are completely defined for normal applications by volatility, vapor pressure, and to a lesser extent, specific gravity. The last by itself has little significance and can only give an indication of quality characteristics when combined with values for volatility

and vapor pressure. It is important for stock quantity calculations and is used in connection with transport and storage. Volatility is expressed in terms of the temperature at which 95% of the material is evaporated. It gives a measure of the least volatile component present. Vapor pressure is related to the more volatile components present. It therefore gives a measure of the most extreme low temperature conditions under which initial vaporization can take place.

By setting limits to vapor pressure and volatility jointly, the specification serves to ensure essentially single-component products for the butane and propane grades. By combining vapor pressure/volatility limits with specific gravity for propane-butane mixtures, essentially two-component systems are ensured.

Hydrocarbon composition

Clauses are included to limit the amounts of minor constituents. These may relate to groups of hydrocarbon derivatives or to specific compounds. Thus limits are set to the total amount of C_2 , C_4 , or C_5 hydrocarbon derivatives and to ethylene in particular, to total dienes and total acetylenes.

By limiting the amount of hydrocarbon derivatives that are lower-boiling than the main component, the vapor pressure control is reinforced. The limitation on the amount of higher-boiling hydrocarbon derivatives supports the volatility clause. The vapor pressure and volatility specifications will often be met automatically if the hydrocarbon composition is correct.

The amount of ethylene is limited for two reasons. Firstly, it may be desirable to restrict the amount of unsaturated components so as to avoid the formation of polymerization deposits. Secondly, the restriction constitutes an additional volatility clause. Ethylene is more volatile than ethane, and therefore, a product with all its C_2 hydrocarbon derivatives in the form of ethylene will have a higher vapor pressure and volatility than one in which the two-carbon constituents are entirely ethane. Both could, however, meet the relevant C_2 clause.

Acetylene is an undesirable constituent because of its corrosive action on copper. A further point, less significant because of the low concentration of acetylene, is that acetylene is more explosive than the other hydrocarbon derivatives present. Butadiene is also undesirable because it may produce deposits that will cause blockages.

Sulfur, sulfur compounds, and corrosion of copper

The following may be defined by a specification: total (volatile) sulfur, carbonyl sulfide, hydrogen sulfide, mercaptan, and copper corrosion.

The manufacturing processes for liquefied petroleum gas are such that most sulfur compounds are removed. The total sulfur level is therefore considerably lower than for other crude oil fuels. A maximum limit for sulfur content helps to define the product more completely. The sulfur compounds that are mainly responsible for corrosion are hydrogen sulfide, carbonyl sulfide, and sometimes elemental sulfur. Hydrogen sulfide and mercaptans have distinctive unpleasant odors.

Control of the total sulfur content, hydrogen sulfide, and mercaptans ensures that the product is not corrosive or nauseating. Stipulating a satisfactory copper strip test further ensures the control of the corrosion.

Residue

The presence of any component substantially less volatile than the main constituents of the LPG will give rise to unsatisfactory performance. It is difficult to set limits to the amount and nature of the residue which will make a product unsatisfactory. Obviously, small amounts of oily material can block regulators and valves. In liquid vaporizer feed systems, even gasoline-type material could cause difficulty.

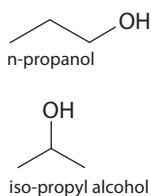
The residue as determined by the End Point Index (EPI) endeavors to give a measure of the higher-boiling hydrocarbon derivatives, but the relationship between EPI, hydrocarbon range, and performance is not established. Other methods are available which measure residue more directly, and for particular applications, it may be possible to relate the values obtained to the performance required and so set satisfactory limits.

Moisture and water

It is a fundamental requirement that any LPG should not contain free water. Dissolved water may give trouble by forming hydrates and giving moisture vapor in the gas phase. Both of these will lead to blockages. It is therefore necessary to limit the amount of dissolved water also.

Propanol

Propanol alcohol (propyl alcohol) is a three-carbon alcohol that has two isomers: (i) 1-propanol, *n*-propanol, or propan-1-ol: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, and (ii) 2-propanol, iso-propyl alcohol, isopropanol, or propan-2-ol: $(\text{CH}_3)_2\text{CHOH}$:

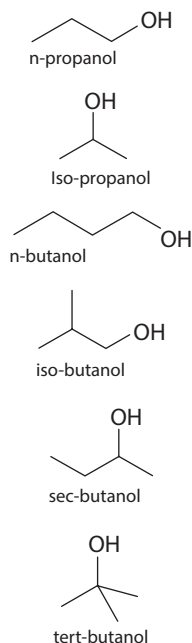


Both compounds are widely used as solvents and as intermediates in the production of various esters and amides. Isopropanol is also used as a disinfectant in pharmaceutical products or as an antifreeze. Currently, the main application of propanol today is for the synthesis of propylene which is an important building block in chemical industries. Propanol as a biofuel has received some attention in alcohol mixtures such as in isopropanol–butanol–ethanol fermentation.

See also: Propanol and Butanol.

Propanol and Butanol

Propanol (propyl alcohol) and butanol (butyl alcohol) exist in various isomeric (structural) forms – isomers are ions or molecules with identical formulas but distinct structures. Thus, for propanol and butanol, the isomers are *n*-propanol, isopropanol (or iso-propanol), *n*-butanol, iso-butanol (more often referred to as *sec*-butanol or secondary butanol), and tertiary-butanol. The various structures are as follows:



The unmodified term *butanol* usually refers to the straight chain isomer with the alcohol functional groups at the terminal carbon, which is also known as *n*-butanol or 1-butanol. The straight chain isomer with the alcohol at an internal carbon is *sec*-butanol or 2-butanol. The branched isomer with the alcohol at a terminal carbon is iso-butanol (isobutanol) or 2-methyl-1-propanol, and the branched isomer with the alcohol at the internal carbon is tert-butanol or 2-methyl-2-propanol. These two alcohols are considerably less toxic and less volatile than methanol. In particular,

butanol has a high flash point of 35°C (95°F), which is a benefit for fire safety, but may be a difficulty for starting engines in cold weather. Propanol and butanol are considerably less toxic and less volatile than methanol. In particular, butanol has a high flashpoint of 35°C, which is a benefit for fire safety, but may be a difficult for starting engines in cold weather.

Also, the different isomers forms can cause subtle-to-significant differences in the properties of the respective isomers. For example, the butanol isomers have different melting and boiling points. *n*-butanol and isobutanol have limited solubility in water (73 g/L at 25°C); *sec*-butanol has substantially greater solubility in water (290 g/L), while *tert*-butanol is miscible with water above the melting point of *tert*-butanol. The hydroxyl group makes the molecule polar, promoting solubility in water, while the longer hydrocarbon chain mitigates the polarity and reduces solubility.

The fermentation processes to produce propanol and butanol from cellulose are fairly tricky to execute, and the *Clostridium acetobutylicum* currently used to perform these conversions produces an extremely unpleasant smell, and this must be taken into consideration when designing and locating a fermentation plant. This organism also dies when the butanol content of whatever it is fermenting rises to 7%. For comparison, yeast dies when the ethanol content of its feedstock hits 14%. Specialized strains can tolerate even greater ethanol concentrations – the so-called turbo yeast can withstand up to 16% ethanol. However, if ordinary *Saccharomyces* yeast can be modified to improve its ethanol resistance, scientists may yet one day produce a strain of the Weizmann organism with a butanol resistance higher than the natural boundary of 7%. This would be useful because butanol has a higher energy density than ethanol, and because waste fiber left over from sugar crops used to make ethanol could be made into butanol, raising the alcohol yield of fuel crops without there being a need for more crops to be planted.

See also: Alcohols, Ethanol, Butanol, Methanol, Propanol.

Proteins

Proteins are nitrogen-containing organic substances which occur in the protoplasm of all plant and animal cells. The composition of proteins varies with the source.

The characteristic structural feature of proteins is a chain (or ring) of amino acids joined together by amide linkages. Peptides are, in effect, a similar class of compounds, but the distinction between a protein and a peptide is not always clear. One arbitrary choice is to use a molecular weight of 10,000 as a distinction between the two classes with proteins having a molecular weight in excess of 10,000 while peptides have a molecular weight below this value.

The distinction might also be made in terms of differences in physical properties such as the degree of hydration and spatial arrangement of the molecules. For example, the naturally occurring peptides have relatively short, flexible chains and, although hydrated in aqueous solution, can be reversibly dehydrated. On the other hand, proteins have long chains which have definite conformational character with water molecules filling the interstices.

The special character of proteins derives not only from the length and complexity of the chains but also from the way in which they are synthesized by organisms in an often metastable form that can be easily and conveniently altered (denatured). The three-dimensional (spatial) character of proteins has an interesting arrangement that involves an alpha-helix.

The principal feature of this helix is the coiling of peptide chains in such a way as to form a hydrogen bond between the amide hydrogen and the carbonyl group at spatially convenient points in the chain. Such bonds are due to the polarization of various organic functional groups where adjacent hydrogen is positively polarized and a heteroatom (an atom other than carbon and hydrogen, usually oxygen) is negatively polarized. The strengths of these bonds are usually on the order of 5 to 10 kcal compared with 60 to 100 kcal for the conventional organic sigma-bonds. There is the potential for the formation of much more stable hydrogen bonds within the protein helix resulting in the formation of ring systems which tend to confer an additional stability (10 to 20 kcal) on the system.

The amino acid side chains lie outside the coil of the helix. Not all proteins are perfect alpha-helices since the steric effects between certain amino acid side chains may be sufficient to influence the stability of the helix.

Proteins occur throughout nature in a wide variety of sizes and shapes, and many proteins contain metals such as iron, zinc, and copper which, in turn, are intimately involved in the physiological (biological) functions of the molecules to which they are bound.

Protium

Hydrogen has three naturally occurring isotopes, sometimes denoted ¹H (sometimes referred to as protium, hydrogen-1), ²H (deuterium, hydrogen-2), and ³H (tritium, hydrogen-3) (Table P-14). The first two of these isotopes are stable, while tritium has a half-life of 12.32 years. The symbols D and T are sometimes used for deuterium and tritium, respectively.

Table P-14 The isotopes of hydrogen.

Isotope	Description
Protium	Ordinary hydrogen with one proton and one electron in the atom. When two atoms of protium are combined with one atom of oxygen, water is created.
Deuterium	Sometimes called “heavy hydrogen,” a non-radioactive isotope that has a neutron in the atom, in addition to the proton and electron. Water made with this isotope is called “heavy water.”
Tritium	A radioactive isotope of hydrogen that has two neutrons in addition to the proton and the electron. Water made with this isotope is called tritium oxide. Tritium is the only one of the three hydrogen isotopes that is radioactive.

The ¹H isotope is the most common hydrogen isotope with an abundance of more than 99.98%. The nucleus of this isotope consists of only a single proton which has never been observed to decay and is, therefore, considered to be a stable isotope. To date, experiments have shown that the minimum proton half-life is in excess of 10³⁴ years.
See also: Deuterium, Hydrogen, Tritium.

Proton

A proton is a subatomic particle (symbol p or p⁺), with a positive electric charge of +1e elementary charge and a mass slightly less than that of a neutron. Protons and neutrons, each with masses of approximately one atomic mass unit, are collectively referred to as nucleons (i.e., particles present in atomic nuclei).
One or more protons are present in the nucleus of every atom and are a necessary part of the nucleus. The number of protons in the nucleus is the defining property of an element, and is referred to as the atomic number (represented by the symbol Z), and, since each element has a unique number of protons, each element has its own unique atomic number.
See also: Electron, Periodic Table of the Elements.

Proven Reserves

Proven reserves (proved reserves) are those reserves of crude oil that are actually found by drilling operations and are recoverable by means of current technology (Table P-15). They have a high degree of accuracy and are frequently updated as the recovery operation proceeds.

Table P-15 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

The proven reserves may be updated by means of reservoir characteristics, such as production data, pressure transient analysis, and reservoir modeling.

Proven reserves are reserves considered to have a 90% probability of being recoverable. Unproven reserves are not deemed recoverable, due to regulatory or economic factors. This class of reserves is further broken down into (i) probable reserves and (ii) possible reserves. Probable reserves are reserves that have an estimated confidence level of approximately 50% of being successfully recovered, while possible reserves are those reserves with only a 10% probability of recovery.

If deterministic methods are used, the term reasonable certainty is intended to express a high degree of confidence that the quantities will be recovered. If probabilistic methods are used, there should be at least a 90% probability that the quantities actually recovered will equal or exceed the estimate.

Proximate Analysis

The proximate analysis test methods were originally developed as a part of the assay of coal but can be applied to many other carbonaceous materials. By definition, the proximate analysis separates the products into four groups which are (i) the moisture content, (ii) the volatile matter production which is often erroneously referred to as volatile matter content even though the unprocessed sample does not contain volatile matter, consisting of gases and vapors driven off during pyrolysis, (iii) the fixed carbon, the non-volatile fraction of the sample, and (iv) ash which is the inorganic residue remaining after combustion and is a reflection of the mineral matter content of the sample. On occasion, proximate analysis may also include ash fusion temperature.

A typical proximate analysis includes the moisture, ash, volatile matter, and fixed carbon contents. Fixed carbon is the material, other than ash, that does not vaporize when heated in the absence of air. It is usually determined by subtracting the sum of the first three values – moisture, ash, and volatile matter – in weight percent from 100%) and is important for economic reasons to know the moisture and ash contents of a coal because they do not contribute to the heating value of a coal. In most cases, ash becomes an undesirable residue and a source of pollution, but for some purposes (*e.g.*, use as a chemical feedstock or for liquefaction), the presence of mineral matter may be desirable. Most of the heat value of a coal comes from its volatile matter, excluding moisture, and fixed carbon content. For most coals, it is necessary to measure the actual amount of heat released upon combustion [expressed in British thermal units (BTUs) per pound or megajoules per kilogram].

The methods of analysis associated with the proximate analysis is, in fact, a combination of the determination of each of three of the properties and calculation of a fourth. Moisture, volatile matter, and ash are all determined by subjecting the sample to prescribed temperature levels for prescribed time intervals. The losses of weight are, by stipulation, due to loss of moisture and, at the higher temperature, loss of volatile matter. The residue remaining after ignition at the final temperature is called ash. Fixed carbon is the difference of these three values summed and subtracted from 100.

The term volatile matter content is actually a misnomer insofar as the majority of the volatile matter is the volatile product of the thermal decomposition of coal through the application of high temperatures. Relative yields and boiling point profiles provide the extent to which natural molecules contribute to the volatile matter without any influence from high-temperature cracking.

The final results of the proximate analysis are usually reported to the first decimal place. The final report of the analysis should always contain the results on a basis of air-dried coal (*i.e.*, coal in its most stable condition and in which it was analyzed), but for purposes of classification or comparison, it is often necessary to convert to another basis such as dry sample, dry-ash-free sample, or as received sample.

P-Series Fuels

A P-series fuel is a blend of natural gas liquids, ethanol, hydrocarbon derivatives, methyl tetrahydrofuran ($\text{CH}_3\text{C}_4\text{H}_7\text{O}$) and is a biomass-derived product. These fuels are clear, colorless liquid blends (octane number: 89-93) that are formulated to be used in flexible fuel vehicles. Like gasoline, low vapor pressure formulations are produced to prevent excessive evaporation during summer and high vapor pressure formulations are used for easy starting in the winter.

Also, these fuels are at least 60% non-crude oil constituents and the majority of the components that make up P-series fuels come from domestically produced renewable resources.

The P-Series fuels provide significant emissions benefits over reformulated gasoline. Each unit of P-series fuel emits approximately 50% less carbon dioxide, 35 % less hydrocarbon derivatives, and 15% less carbon monoxide than gasoline. The fuel also has 40% less ozone-forming potential. The other gasoline-substitute ether, MTBE (methanol tertiary butyl ether) is a crude oil-derived product and is made from isobutene [$(\text{CH}_3)_2\text{CH}=\text{CH}_2$ and methanol]. The P-series fuel emissions are generally below those for reformulated gasoline and are well below federal emissions standards. P-series fuels join the list of alternatives to gasoline that includes ethanol (E85), methanol (M85), natural gas, propane, and electricity.

See also: Fuels.

Pullman-Kellogg Process

The Pullman-Kellogg molten salt process is a process that was developed for the gasification of coal but which has the potential to be adaptable to other carbonaceous feedstocks. In the process, air is bubbled into the bottom of the gasifier through multiple inlet nozzles and the feedstock (sized to 1/4 in.; 6 mm) is fed beneath the surface of the molten salt bath using a central coal feed tube whereupon natural circulation and agitation of the melt disperses the coal.

The main gasification reaction is a partial oxidation reaction, and volatile matter in the feedstock reacts to produce a fuel gas free of oils, tars, as well as ammonia. A water-gas shift equilibrium exists above the melt, and, accordingly, in the reducing environment, carbon dioxide and water concentrations are minimal. Sulfur in the coal reacts with the melt to form sodium sulfide.

See also: Biomass Gasification, Gasifiers.

Pulping

Like delignification, pulping is another method by which wood is prepared for use in other areas but which also has potential in preparing wood for conversion to fuels and other chemicals.

In a chemical pulping process, heat and chemicals are added to wood chips in a pressure cooker called the digester. In the kraft process, an aqueous solution of sodium hydroxide and sodium sulfide, known as white liquor, selectively dissolves the lignin and make it soluble in the cooking liquid. After 2 to 4 hours, the mixture of pulp, spent pulping chemicals, and wood waste is discharged from the digester. The pulp is washed to separate it from the black liquor – the pulping chemicals and wood waste. Kraft pulping is a low yield process – approximately 45% w/w of the wood used becomes pulp. The pulp, called brown stock at this point in the process, is ready to be bleached. Softwood pulp from a conventional cooking process contains approximately 4.5% lignin. This lignin will be removed, and the pulp will be brightened during the bleaching process.

Efficient pulp washing is important because it ensures the maximum recovery of the pulping chemicals and it minimizes the amount of organic waste carried over with the pulp into the bleaching process. Poorly washed pulps require higher bleaching chemical doses, thus increasing the cost and the amount of organic waste discharged in the bleach plant effluent.

The chemical recovery process has four steps which are (i) the water from the washer goes to the evaporator, where the black liquor is concentrated to 65% to 75% solids prior to its entry to the recovery boiler, (ii) in the recovery boiler, a specially-designed furnace, the used pulping chemicals are separated from the wood waste – the pulping chemicals form a lava-like smelt at the base of the recovery boiler; the wood waste is burned at the top of the recovery boiler, and this heat is used to generate high-pressure steam, which can be used to meet the steam and electricity requirements of the process, (iii) the smelt is poured into a large tank of water to form green liquor, a mixture of sodium sulfide and sodium carbonate, and (iv) lime addition, which involves the addition of calcium oxide to the green liquor to convert the sodium carbonate into sodium hydroxide, and thus remake the white liquor; the resulting calcium carbonate is converted back to lime in a lime kiln.

Conventional pulping processes remove approximately 95% w/w of the lignin from the pulp. In the past, the remaining lignin was removed during the bleaching process. Oxygen has been used to remove lignin from pulp on

a mill scale since the late 1970s. Scandinavian mills first installed oxygen delignification in response to concerns related to the amount of organic waste in the effluent. Union

The pulp is washed after it leaves the tower where it has reacted with oxygen. The wastewater or filtrate can either be used in the brown stock washers, or it can be routed directly to the evaporator where it will be combined with the black liquor. The degraded lignin products will be burned for energy in the recovery boiler, so less organic waste will be discharged in the waste water from the bleach plant.

Digesters can be modified to remove more lignin from the pulp without damaging the cellulose by using the same amount of white liquor, but adding it at several points during the cooking process. This additional wood waste is also sent to the recovery system.

Extended delignification and oxygen delignification are proven technologies that can remove as much as 70% of the lignin before the bleaching process removes the remaining lignin and colored substances. To produce high-quality totally chlorine-free pulp (TCF), mills will have to install oxygen delignification, extended delignification, or both in order to minimize the use of chemicals in the bleach plant. More organic waste is burned in the recovery boiler, and smaller quantities of bleaching chemicals are required.

Pulpwood

Pulpwood is round wood, whole-tree chips, or wood residues that are used for the production of wood pulp. The composition of pulpwood varies with the source trees (Table P-16).

Table P-16 Examples of the chemical constituents of pulpwood.

Wood	Cellulose	Lignin	Xylan	Other
Aspen	56.5	16.3	16.0	11.2
Balsam fir	47.4	29.4	4.8	15.4
Birch	44.5	18.9	24.6	12.0
Jack Pine	45.0	28.6	7.1	19.3
Maple	44.8	24.0	17.3	13.9
White spruce	48.5	27.1	6.8	17.6

Pulpwood is also used as the raw material for some wood products, such as oriented strand board (OSB), and there is an increasing demand for pulpwood as a source of bio-energy. Trees raised specifically for pulp production account for 16% of world pulp production, old growth forests 9% and second- and third- and more generation forests account for the balance. Reforestation is practiced in most areas, so trees are a renewable resource.

In the logging of mixed forest stands, the better trees are usually used for sawlogs for lumber production, while the inferior trees and components are harvested for pulpwood production. Pulpwood usually derives from four types of woody materials in a mixed logging operation: (i) open-grown trees, that are heavily branched low on the trunk, and so make poor sawlogs, (ii) dead or diseased trees, (iii) tops cut from trees harvested for sawlogs (branches are rarely used since they contain little usable wood after the bark has been removed), and (iv) trees too small to harvest for sawlogs.

Pulpwood is also harvested from plantations/tree farms established for the specific purpose of growing pulpwood, with little or minimal sawlog production. Monocultures of species intended specifically for pulpwood include loblolly/slash pine in the southern USA; various species of eucalyptus (most commonly *Eucalyptus globulus* and *Eucalyptus grandis*) in Latin America, the Iberian Peninsula, Australia, south-east Asia, and southern Africa and acacia (most commonly *Acacia mangium*) in south-east Asia and southern Africa.

Natural forest stands may also be harvested solely for pulpwood where, for various reasons, the value of the trees as sawlogs is low. This may be due to the predominant species in the forest stand (for example, some aspen forests in northern North America), or to the relative proximity of the nearest sawmill or pulp mill.

Pulpwood trees are any commercial tree species that does not have the size or quality to make other wood products. This includes large trees with defects or multiple branches eliminating sawtimber possibilities and trees too

small to be cut for sawtimber. Pulpwood trees have to be at least 5 inches diameter at breast height (dbh) and do not bring as much money to the as sawtimber size trees.

Salvage cuts after forest fires, tornadoes, hurricanes, or other natural disasters are often also for pulpwood. An alternative source of wood for use in kraft pulping is recovered lumber from demolition, industrial processing of wood, and wooden pallets.

See also: Logs and Woodchips, Wood.

Puraspec Process

The Puraspec processes use fixed beds of catalysts and chemical absorbents to remove traces of contaminants from hydrocarbon gases and liquids. In particular, the processes are designed to remove mercury and a range of sulfur compounds – most frequently hydrogen sulfide (H_2S) and carbonyl sulfide (COS). Mercury removal from hydrocarbon streams is a stringent requirement in order to avoid corrosion of equipment, poisoning of catalysts, and to comply with environmental regulations.

The processes are used for *sweetening* to meet pipeline specifications and *polishing* to meet individual feedstock requirements. The fixed beds of chemical absorbents provide effectively total irreversible selective removal of impurities from wet or dry hydrocarbon derivatives without feedstock losses.

See also: Gas Cleaning, Gas Processing.

Purisol Process

The Purisol process is designed for the selective desulfurization of raw gas streams (including natural gas) from various processes.

In the process, N-Methyl-2-Pyrrolidone (NMP) is used as physical solvent. The solvent absorbs the undesired components carbon disulfides, hydrogen sulfide, carbonyl sulfide, hydrogen cyanide, and ammonia as well as carbon dioxide. These components are subsequently desorbed by reducing the pressure and reboiling the solvent.

As the solubility of hydrogen sulfide is significantly higher than that of carbon dioxide, little carbon dioxide is co-absorbed. Consequently, Claus gas with particularly high concentrations of hydrogen sulfide can be produced. Hydrogen cyanide and higher- molecular-weight sulfur compounds are also discharged into the Claus gas. The solubility increases steeply as the temperature decreases. For this reason, absorption is performed at low temperatures, while high temperatures are used for regeneration.

Where required, impurities such as hydrogen cyanide or higher-molecular-weight sulfur compounds are removed from the cooled raw gas in a prewash stage of the absorber. In the main absorber section, the sulfur compounds, in particular hydrogen sulfide, are removed from the raw gas until reaching the admissible residual concentration.

The solvent from the hot regeneration, which has been subsequently cooled, is added at a temperature ranging between ambient temperature and $-10^{\circ}C$. Before the desulfurized clean fuel gas leaves the absorber, traces of NMP can be removed in a water wash.

The solvent from the hydrogen sulfide absorber contains large quantities of hydrogen sulfide and little carbon dioxide. It is relieved to a lower pressure in the bottom section of the reabsorber, whereby carbon dioxide and small quantities of hydrogen sulfide are desorbed. The solvent from the hot regeneration in the upper section of the reabsorber immediately reabsorbs the hydrogen sulfide. As a consequence, sulfur-free gas leaves the reabsorber, which can either be rerouted to the raw gas stream or used as fuel gas.

The solvent from the reabsorber is heated and further flashed in the hot flashing stage. Any carbon dioxide removed in this stage is returned to the reabsorber. The solvent leaving the hot flashing stage is completely regenerated by reboiling in the lower part of the hot regeneration. The hydrogen sulfide-rich gas is then routed to the downstream Claus unit. An adequate adjustment of pressures and temperatures allows for extremely high concentrations of hydrogen sulfide.

The gas rich in hydrogen sulfide is processed in a Claus plant and a hydrogenation unit, yielding pure sulfur from hydrogen sulfide. The sulfur compounds produced in the Claus process are converted to hydrogen sulfide by adding

hydrogen in the hydrogenating unit. The exhaust gas from hydrogenation is cooled to condense the water contained in the gas. The gas is then returned to the reabsorber to be completely desulfurized.

Since the process reduces the sulfur content in the fuel gas to only a few ppm hydrogen sulfide, high desulfurization efficiency can be achieved. If the raw gas contains material quantities of carbonyl sulfide, they have to be treated by catalytic hydrolyzation before the hydrogen sulfide wash.

See also: Gas Cleaning.

Purox Process

The Union Carbide PUROX process employs a partial oxidation process using oxygen for converting municipal solid waste to fuel gas and inert slag.

This conversion is accomplished by (i) shredding and preparing the refuse for conversion, (ii) producing a gas of low calorific value from the refuse, and (iii) methanation of the off-gas to a quality suitable for sale in the existing gas distribution system.

The principal component of the Purox system is a vertical shaft reactor. Solid waste, either raw or processed, is introduced into the top of the furnace and via an airlock feeder. Simultaneously, pure oxygen is forced into the base of the column at the rate of approximately 0.2 Mg per Mg of solid waste. Char formed from the solid waste reacts with the incoming oxygen, generating temperatures on the order of 1,370 to 1,660°C (2,500 to 3,020°F). Gases formed in the reaction between the oxygen and the char ascend to the top of the retort, countercurrently to the incoming waste. In the process, the combustion of the gases supplies the energy required to drive the pyrolysis reaction. As the gases approach the top of the retort, they dry the incoming waste and, consequently, are further cooled to approximately 90°C (195°F). The off gas contains certain impurities that are removed in a gas cleaning system, which consists of an electrostatic precipitator, an acid absorption column, and a condenser.

Low-Btu off-gas, with a heating value of 590 Btu/ft³, to synthetic natural gas (SNG), which is comprised mostly of methane and which has a heating value of 879 Btu/ft³. Upgrading is accomplished by a series of clean-up and catalytic conversion steps.

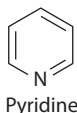
The clean-up steps encompass a benzol wash for removal of residual hydrocarbon liquids from the off-gas, sulfur and chloride removal, carbon dioxide removal, and dehydration. The catalytic conversion steps consist of hydrogenation and methanation.

Approximately one ton of refuse requires approximately 0.2 ton of oxygen and produces 0.7 ton of medium Btu fuel gas, 0.22 ton of sterile residue, and 0.28 ton of wastewater. Refuse, preprocessed for recovery of iron and other materials, is fed to the top of a vertical shaft furnace through a gas seal, and oxygen is injected into the bottom hearth section. The reaction of oxygen with char formed from the particles of refuse generates high temperatures which melt glass, metal, and other materials. Hot gases from this process are used to pyrolyze the refuse, and the resulting fuel gas is cleaned. A gas analysis and slag analysis are provided, and several features of the system are discussed.

See also: Combustion, Gasification, Gasification of Biomass.

Pyridine Bases

Pyridine is a basic heterocyclic organic compound with the chemical formula C₅H₅N. It is structurally related to benzene, with one methine group replaced by a nitrogen atom.



Pyridine is a highly flammable, weakly alkaline, water-miscible liquid with a distinctive, unpleasant fish-like smell.

The nitrogen center of the pyridine molecule features a basic lone pair of electrons which does not overlap with the aromatic π -system ring; consequently pyridine is basic, having chemical properties similar to those of tertiary amines.

In addition to ammonia, a gas stream may contain small quantities of miscellaneous compounds which may be removed for their own value or to improve the gas product; among the more common of these are pyridine bases and hydrogen cyanide. The former are nitrogen-containing organic materials which belong to the pyridine series (C_5H_5N) and which occur in coal tar. They can be removed from the gas by reaction with sulfuric acid, which converts the bases to nonvolatile sulfate derivatives, and the pyridine derivatives can be recovered as a valuable by-product from the scrubber liquor by neutralizing the liquor with ammonia followed by steam distillation of the uncharged bases. The condensate is saturated with ammonium sulfate, which reduces the solubility of the uncharged bases and causes them to precipitate from solution.

See also: Heteroatom Compounds, Polynuclear Aromatic Hydrocarbons.

Pyrolysis

Pyrolysis (also called devolatilization) is the process of the thermal decomposition of biomass at high temperatures (greater than 205°C, 400°F) in the absence of air; the end product of pyrolysis is a mixture of solids (char), liquids (oxygenated oils), and gases (methane, carbon monoxide, and carbon dioxide) with proportions determined by operating temperature, pressure, oxygen content, and other conditions (Table P-17)

Table P-17 Products of pyrolysis and potential uses.

Feedstock	Primary product	Secondary product
Biomass, waste	Gases	Fuel gas
		Synthesis gas
	Bio-oil	Fuel oil
		Convert to gasoline
		Convert to diesel fuel
	Char	Solid fuel
		Activated carbon
		Filler

When carbonaceous materials, such as biomass, are pyrolyzed, hydrogen-rich volatile matter is distilled and a carbon-rich solid residue is left behind. The carbon and mineral matter remaining behind is the residual char. In this regard, the term carbonization is sometimes used as a synonym for coal pyrolysis.

However, carbonization has as its aim the production of a solid char, whereas in synthetic fuel production, the greatest interest centers on liquid and gaseous hydrocarbon derivatives.

Pyrolysis is one method to produce liquid fuels from biomass. Moreover, as gasification and liquefaction are carried out at elevated temperatures, pyrolysis may be considered a first stage in any conversion process. The study of pyrolysis can be dated from the end of the eighth century when Arabian scientists produced liquids from bitumen. Despite the many advances in understanding achieved since that time, there is still not a unified fundamental picture of the complex chemical and physical phenomena that take place, which given the raw material and the physical conditions of heating, would enable a unique determination of the products.

Of most interest in the production of synthetic fuels from biomass is the prediction of the rate and amount of volatile yield and product distribution for a given raw material and the set of pyrolysis conditions. Among the important chemical variables are the elemental composition and chemical composition. Above 100°C and below 300°C, the evolution of volatile matter is not large and the volatile material is composed of oxides of carbon and water. In the active or second stage of decomposition, approximately 75% of all the volatile matter ultimately released is evolved. In the third stage, there is a secondary degasification associated with the transformation of the char, accompanied by the release of non-condensable gases, mainly hydrogen.

In all stages of pyrolysis, but particularly the higher temperature ones, it is important to distinguish between the primary volatile products of decomposition and those products which result from secondary cracking and coking reactions and from gasification reactions such as between the char and evolved water.

The effect of heating rate on the amount and composition of pyrolysis volatile yields has been an important issue.

The relative quantity of char, tars, and gases evolved on pyrolysis is strongly dependent both on the rate of heating and the final temperature attained. Slow-heating, low temperature pyrolysis favors char yields. In theory, cellulose can be carbonized to yield carbon and water only. In practice, the initial decomposition product of cellulose pyrolysis is levoglucosan, $C_6H_{10}O_5$, an anhydride of glucose. Subsequent coking and cracking reactions result in a char that contains oxygen and hydrogen in addition to the carbon. The char remaining on pyrolysis of wood contains approximately 80% carbon, 17% oxygen, and 3% hydrogen.

Particle size is known to influence pyrolysis yield. This effect may be related to heating rate, in that larger particles will heat up more slowly, so the average particle temperatures will be lower, and hence volatile yields may be expected to be less. If the particle size is sufficiently small, it will be heated uniformly. When finely ground carbonaceous particles are heated rapidly, larger yields than the functional composition of the organic and inorganic matter, as well as the composition of the ambient gas in which the pyrolysis takes place. Among the more important basic physical variables are the final temperature, the time and rate of heating, the particle size distribution, the type and duration of any quenching, and the pressure. An indication of the uncertainty existing in this field is that at present, there is no agreement on whether yield, which is the loss in mass of the raw material from pyrolysis, is changed with heating rate.

The composition of the volatile products evolved in pyrolysis is largely determined by the raw organic material. In the case of biomass, at 500°C, the major constituents of the gas include carbon oxides, methane, hydrogen, and low molecular weight along with hydrogen sulfide and ammonia.

Pressure may be expected to affect volatile yields, with higher pressures reducing the yields and lower ones increasing them. However, higher pressures favor cracking reactions, so high pressure will produce a larger volume of low-boiling hydrocarbon derivative (gases), whereas lower pressure will lead to higher yields of high-boiling (often viscous) oil fractions and tar.

Pyrolysis in a hydrogen atmosphere, termed *hydropyrolysis*, can increase the volatile yield and proportion of lower-molar-mass hydrocarbon derivatives. Hydropyrolysis is defined to include thermal decomposition and the attendant hydrogenation but not the hydrogasification of the char. Hydrogen reacts much faster with decomposing organic material and with the primary volatiles than with residual char. The increase in volatile yield is attributable to the hydrogenation of free radical fragments sufficient to stabilize them before they react and form char.

Rapid pyrolysis (fast pyrolysis) involves the collection of the volatile matter and depending on the temperature of the process these materials can be combusted. This liquid product has the potential to be used as fuel oil. Temperatures range from 800 to 900°C. Fast pyrolysis can leave as little as 10% char and can convert as much as 60% into a gas.

See also: Bio-oil, Thermal Decomposition.

Pyrolysis – Biomass

Pyrolysis of biomass at high temperatures (greater than 205°C, 400°F) in the absence of air results in a mixture of (i) gases, such as methane, carbon monoxide, and carbon dioxide, (ii) liquids, such as oxygenated oils, and (iii) solids, often referred to as char), with proportions determined by operating temperature, pressure, oxygen content, and other conditions.

When carbonaceous materials, such as biomass, are pyrolyzed, hydrogen-rich volatile matter is distilled and a carbon-rich solid residue is left behind. The carbon and mineral matter remaining behind is the residual char. In this regard, the term carbonization is sometimes used as a synonym for coal pyrolysis. However, carbonization has as its aim the production of a solid char, whereas in synthetic fuel production, the greatest interest centers on liquid and gaseous hydrocarbon derivatives. Thus:

Feedstock	Primary product	Secondary product
Biomass, waste	Gases	Fuel gas
		Hydrocarbon gases
		Synthesis gas
	Bio-oil	Fuel oil
		Convert to gasoline
		Convert to diesel fuel
	Char	Solid fuel
		Activated carbon
		Filler

Pyrolysis is one method to produce liquid fuels from biomass. Moreover, as gasification and liquefaction are carried out at elevated temperatures, pyrolysis may be considered a first stage in any conversion process.

The study of pyrolysis can be dated from the end of the eighth century when Arabian scientists produced liquids from bitumen. Despite the many advances in understanding achieved since that time, there is still not a unified fundamental picture of the complex chemical and physical phenomena that take place, which given the raw material and the physical conditions of heating would enable a unique determination of the products.

Of most interest in the production of synthetic fuels from biomass is the prediction of the rate and amount of volatile yield and product distribution for a given raw material and the set of pyrolysis conditions. Among the important chemical variables are the elemental composition and chemical composition. Above 100°C and below 300°C, the evolution of volatile matter is not large and the volatile material is composed of oxides of carbon and water. In the active or second stage of decomposition, approximately 75% of all the volatile matter ultimately released is evolved. In the third stage, there is a secondary degasification associated with the transformation of the char, accompanied by the release of non-condensable gases, mainly hydrogen.

In all stages of pyrolysis, but particularly the higher temperature ones, it is important to distinguish between the primary volatile products of decomposition and those products which result from secondary cracking and coking reactions and from gasification reactions such as between the char and evolved water.

The effect of heating rate on the amount and composition of pyrolysis volatile yields has been an important issue.

The relative quantity of char, tars, and gases evolved on pyrolysis is strongly dependent both on the rate of heating and the final temperature attained. Slow-heating, low temperature pyrolysis favors char yields. In theory, cellulose can be carbonized to yield carbon and water only. In practice, the initial decomposition product of cellulose pyrolysis is levoglucosan, $C_6H_{10}O_5$, an anhydride of glucose. Subsequent coking and cracking reactions result in a char that contains oxygen and hydrogen in addition to the carbon. The char remaining on pyrolysis of wood contains approximately 80% carbon, 17% oxygen, and 3% hydrogen.

Particle size is known to influence pyrolysis yield. This effect may be related to heating rate, in that larger particles will heat up more slowly, so the average particle temperatures will be lower, and hence volatile yields may be expected to be less. If the particle size is sufficiently small, it will be heated uniformly. When finely ground carbonaceous particles are heated rapidly, larger yields than the functional composition of the organic and inorganic matter, as well as the composition of the ambient gas in which the pyrolysis takes place. Among the more important basic physical variables are the final temperature, the time and rate of heating, the particle size distribution, the type and duration of any quenching, and the pressure. An indication of the uncertainty existing in this field is that at present, there is no agreement on whether yield, that is the loss in mass of the raw material from pyrolysis, is changed with heating rate.

The composition of the volatile products evolved in pyrolysis is largely determined by the raw organic material. In the case of biomass, at 500°C, the major constituents of the gas include carbon oxides, methane, hydrogen, and low molecular weight along with hydrogen sulfide and ammonia.

Pressure may be expected to affect volatile yields, with higher pressures reducing the yields and lower ones increasing them. However, higher pressures favor cracking reactions, so high pressure will produce a larger volume of low-boiling hydrocarbon gases, whereas lower pressure will lead to larger tar and oil fractions.

Pyrolysis in a hydrogen atmosphere, termed *hydropyrolysis*, can increase the volatile yield and proportion of lower-molar-mass hydrocarbon derivatives. Hydropyrolysis is defined to include thermal decomposition and the attendant hydrogenation but not the hydrogasification of the char. Hydrogen reacts much faster with decomposing organic material and with the primary volatiles than with residual char. The increase in volatile yield is attributable to the hydrogenation of free radical fragments sufficient to stabilize them before they react and form char.

Rapid pyrolysis (fast pyrolysis) involves the collection of the volatile matter, and depending on the temperature of the process, these materials can be combusted. This liquid product has the potential to be used as fuel oil. Temperatures range from 800 to 900°C. Fast pyrolysis can leave as little as 10% char and can convert as much as 60% into a gas.

See also: Pyrolysis Oil, Pyrolysis Processes.

Pyrolysis Processes

In a pyrolysis process, solid biomass (mainly herbaceous) is transformed into a liquid-state semi-finished material – pyrolysis slurry that is fed into the gasifier. Unlike gasification, pyrolysis represents thermal degradation of feedstock in the absence of an externally supplied oxidizing agent. As a result, pyrolysis yields mainly liquids (up to 80% on mass basis via gas condensing) and some tars and chars, while gasification output consists predominantly of gaseous products. For synthesis gas (and biomass-to-liquids) production, flash pyrolysis is typically employed.

Generally, pyrolysis is a medium temperature method which produces gas, oil, and char from crops which can then be further processed into useful fuels or feedstock. Pyrolysis is often considered to be the gasification of biomass in the absence of oxygen, but the chemistry of each process may differ significantly. In general, biomass does not gasify as easily as coal, and it produces other hydrocarbon compounds in the gas mixture exiting the gasifier; this is especially true when no oxygen is used. The products of biomass pyrolysis include gases such as methane, hydrogen, carbon monoxide, carbon dioxide, bio-oil, and char. As a result, typically an extra step must be taken to reform these products with a catalyst to yield a clean synthesis gas mixture of hydrogen, carbon monoxide, and carbon dioxide. Thus, when organic matter is heated at increasing temperatures in open containers, a variety of processes generally occur, in successive or overlapping stages.

Depending upon the operating conditions (temperature, heating rate, particle size and solid residence time), pyrolysis can be divided into three subclasses: conventional, thermal, or catalytic. For example, to maximize bio-oil production, fast/flash pyrolysis is used, heating the biomass to approximately 500°C (930°F) for less than ten seconds. In the pyrolysis of plastics, the macromolecular structures are broken down into smaller molecules (oligomers and monomers); further degradation depends on temperature, residence time, presence of catalysts, and other process conditions. Pyrolysis aims to convert waste into other valuable chemicals, which can be used as feedstock for downstream industrial processes or transportation fuels. The approaches: molten salts, cracking (catalytic, hydrocracking, and thermal), and liquefaction are discussed.

Molten salts such as lithium chloride-potassium chloride with 10% w/w cuprous chloride (LiCl-KCl-10% CuCl) at 520°C (970°F) are used to pyrolyze polymeric waste to yield a fuel oil. At a process temperature of 420°C (790°F), the gaseous fraction is minimized; this enables a higher liquid and solid fraction to be recovered. The recovered fractions consist of low-boiling oils, aromatic derivatives, paraffin waxes, and monomers.

In general, pyrolysis of organic substances produces volatile products and leaves a solid residue enriched in carbon (char) – as an example, pyrolysis is one of the processes involved in the reduction of char from wood. As another example, the process is used frequently in the chemical industry, for example, to produce ethylene, many forms of carbon, and other chemicals from crude oil, coal, and wood, to produce coke from coal. In the current context, other applications of pyrolysis would convert biomass into synthesis gas, waste plastics into usable oil, and char.

Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles and a short hot vapor residence time in the reaction zone. Several reactor configurations have been shown to assure this condition and to achieve yields of liquid product as high as 75% based on the

starting dry biomass weight. They include bubbling fluid beds, circulating and transported beds, cyclonic reactors, and ablative reactors.

Briefly, ablative pyrolysis is conceptually different compared to other fast pyrolysis methods. Most pyrolysis processes depend on having a high heat-transfer rate, which determines the rate of the reaction, and, therefore, these systems employ small biomass particles. Ablative pyrolysis depends on heat transfer from the hot reactor wall to melt the wood particles contacting the wall under pressure. Unlike other pyrolysis processes, because the reaction rates are not limited by heat transfer through the biomass particle, large biomass particles up to lumber size may also be processed by an ablative pyrolysis reactor.

Fast pyrolysis of biomass produces a liquid product (referred to as pyrolysis oil or bio-oil) that can be readily stored and transported. Pyrolysis oil is a renewable liquid fuel and can also be used for production of chemicals. Fast pyrolysis has now achieved a commercial success for production of chemicals and is being actively developed for producing liquid fuels. Pyrolysis oil has been successfully tested in engines, turbines, and boilers, and been upgraded to high-quality hydrocarbon fuels. In the 1990s, several fast pyrolysis technologies reached near-commercial status and the yields and properties of the generated liquid product depend on the feedstock, the process type and conditions, and the product collection efficiency.

The direct hydrothermal liquefaction process involves converting biomass to an oily liquid by contacting the biomass with water at elevated temperatures (300 to 350°C, 570 to 660°F) with sufficient pressure to maintain the water primarily in the liquid phase residence times up to 30 minutes. Alkali may be added to promote organic conversion. The primary product is an organic liquid with reduced oxygen content (approximately 10%), and the primary by-product is water containing soluble organic compounds.

The importance of the provisions for the supply of feedstocks as crops and other biomass is often underestimated since it is assumed that the supplies are inexhaustible. While this may be true over the long term, the short-term supply of feedstocks can be as much as risky as any venture.

Hydrocracking of polymer waste involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures. Typical plastic waste feedstock like polyethylene (PE), polyethylene terephthalate (PET), polystyrene, polyvinyl chloride (PVC), and mixed polymers are reacted in the presence of a catalyst (platinum, nickel, molybdenum, and iron on acid solids such as alumina, zeolites, and sulfonated zirconia) at 150 to 400°C (300 to 750°F) and hydrogen at 3 to 10 MPa to produce a high-quality gasoline.

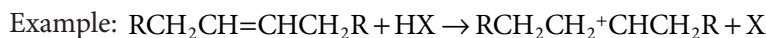
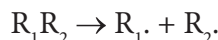
Catalytic cracking involves a suitable catalyst to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. Catalytic degradation yields a narrow product distribution with a peak at lower-molecular-weight hydrocarbon derivatives and occurs at lower temperatures. Using solid acid catalysts, HZSM-5, HY, rare earth metal-exchanged Y-type (REY) zeolite, and silica-alumina for polymeric waste yields 30% w/w gasoline and 20% w/w high-boiling oil. The differences among catalysts arise in the production of coke and gas fractions. Formation of coke is not desirable as it results in catalytic deactivation by fouling and plugging the pore paths. Catalytic cracking, owing to its lower operating temperature, appears to be more technologically sound than thermal pyrolysis; however, it is more costly. The addition of a catalyst enhances the conversion and fuel quality, as compared to pure thermal pyrolysis.

There are numerous proposed mechanisms for catalytic degradation. These include the carbonium ion mechanism and the free radical mechanism. In the carbonium ion (R^+) mechanism, there are four steps: initiation, depropagation, isomerization, and aromatization. In the initiation step, the carbonium ion is generated through proton addition to an olefinic linkage, beta-scission, or through the abstraction of a hydride ion by low-molecular-weight carbonium ions.

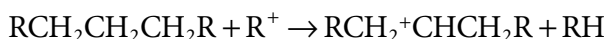
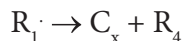
In the depropagation step, the molecular weight of the main polymer chain can be successively reduced through beta-scission. In the isomerization step, the carbonium ion intermediates can undergo a hydrogen atom shift or a carbon atom shift, leading to rearrangement of the molecules. Some of the carbonium ion intermediates can also undergo cyclization reactions, which leads to the formation of aromatics (aromatization step).

In the free radical mechanism, there are the three known radical mechanism steps: initiation, propagation, and termination. Normally, random bond breaking generates a radical in the initiation step after which the radical is propagated via a number of reactions such as beta-scission, radical abstraction, and radical decomposition. Finally, recombination of two radicals leads to the termination step. The sequence can be represented more fully as:

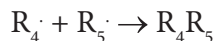
Initiation:



Propagation:



Termination:



Thermal cracking (pyrolysis) involves the degradation of polymeric materials by heating in the absence of oxygen and is usually conducted between 350 and 900°C (650 to 1,650°F). The products formed are a carbonized char and a volatile fraction that may be separated into a condensable hydrocarbon oil consisting of paraffins, iso-paraffins, olefins, naphthenes, aromatics, and a non-condensable high calorific value gas.

The thermal pyrolysis of polymeric waste at temperatures higher than 480°C (895°F) yields a gas-liquid hydrocarbon. At 650 to 760°C (1,200 to 1,400°F), more of the gaseous product is generated; conversely, at lower temperatures, up to 85% of the product is liquid hydrocarbon derivatives. The portion of each fraction and their precise composition depends primarily on the properties of the waste plastic material(s) and the process parameters (temperature, pressure, residence time of the feedstock in the thermal zone). Both the gaseous and the liquid forms of the polymeric waste can be utilized as a feedstock to petrochemical facilities. Generally, thermal cracking results in liquids with low octane value and high residue content at moderate temperatures; this is an inefficient process for producing gasoline ranges. The gaseous products obtained by thermal pyrolysis are not suitable for use as fuel products and require further refining to be upgraded to usable fuel products. A few researchers have sought to improve thermal pyrolysis of waste plastics without employing the use of catalysts. However, these changes either yielded insignificant improvements or added another level of complexity and costs to the system.

Typically, discarded tires can be reduced in size by grinding, chipping, pelletizing, and passed through a classifier to remove the steel belting after which the chips are pyrolyzed for 1 hr at a temperature of 300 to 500°C (570 to 930°F) and then heated for 2 hr in a closed retort. The products are then distilled (purification and analysis) which yields oil and gas and char. However, discarded tires can also be debanded, shredded to 25 mm, and ground to 24 mesh as a feed preparation step for occidental flash pyrolysis which involves flash pyrolysis and product collection. The pyrolytic reaction occurs without the introduction of hydrogen or using a catalyst. This yields a gaseous stream that is passed to a quench tower from which fuel oil and gas (recycled to char fluidized and pyrolysis reactor as a supplemental fuel) and carbon black (35% w/w) is produced.

Hydrothermal liquefaction and pyrolysis are often confused since both are thermochemical processes where organic compounds are converted to liquid products. However, in hydrothermal liquefaction, macro-molecules are decomposed into unstable, reactive low-molecular-weight products in the presence of a catalyst. These fragments repolymerize into high-molecular-weight oily compounds.

The hydrothermal liquefaction process involves solvolysis, decarboxylation, hydrogenolysis, and hydrogenation, leading to challenging mechanistic transformation studies. During solvolysis, the solvent reacts with the molecule, helping to begin the degradation of the biomass. Depolymerization of hemicelluloses, cellulose, and lignin further degrades the biomass to smaller molecules. In decarboxylation, loss of carbon dioxide can lead to rearrangement of

the molecule. Molecules can also be further transformed via hydrogenolysis (water molecules split into a hydrogen ion, H^+ , and a hydroxyl ion, OH^- , and react with feedstock molecules) and hydrogenation (hydrogen is added to the molecule).

Similar to entrained flow gasification, in flash pyrolysis, the residence time of fuel is short – on the order of several seconds. Unlike entrained flow gasification however, the optimum process temperature is much lower – [approximately $500^{\circ}C$ ($930^{\circ}F$)] and the operating pressure is nearly atmospheric – approximately 14.7 psi. The chopped biomass (particles of less than 5 mm) is not heated directly, but with a hot sand medium (similar to fluidized bed gasification) in proportion 1:20, respectively. The pyrolysis gases are cooled down as quickly as possible (in a few seconds) to temperatures below $100^{\circ}C$ ($212^{\circ}F$), and a liquid condensate (pyrolysis oil) is obtained.

The char from pyrolysis is separated from the sand in a cyclone and then milled. The char powder is mixed with the pyrolysis oil, forming a pyrolysis-char slurry, which increases the overall carbon conversion efficiency. The sand separation from the char does not have to be 100% effective since some material of similar type should anyhow be added to the entrained flow gasifier to improve molten slag properties.

Pyrolysis is particularly suitable for herbaceous biomass also because the alternative pre-treatment – fine shredding – is much more difficult and costly compared to that of wood. The pyrolysis slurry feeding into the gasifier with sufficient extent of atomization to ensure full and complete gasification is, however, still a major technical challenge.

Pyrolysis oil is a strong acid which means it is a powerful corrosive substance. Its handling, storage, and transportation therefore require sophisticated and expensive materials, i.e., stainless steel tanks. In addition, there are some concerns related to the potential carcinogenic impact of pyrolysis slurry. The relatively low flash point of pyrolysis oil also imposes additional safety requirements for handling, storage, and transportation.

See also: Carbonization, Pyrolysis, Pyrolysis Oil, Thermal Decomposition.

Pyrolysis Oil

Pyrolysis oil (often referred to as bio-oil and sometimes called bio-crude) is the liquid condensate produced from biomass (forestry residues, crop residues, waste paper and organic waste) by means of processes such as pyrolysis and thermochemical conversion. Depending on the composition of the feedstock and the process, the yield of bio-oil from wood, paper, and other biomass ranges on the order of 60 to 95% w/w wt%. The yield of bio-oil from wood can range from 72 to 80% w/w, depending on the relative amounts of cellulose and lignin in the material. Materials with a high lignin content, such as bark, tend to give lower liquid yields (typically, 60 to 65% w/w), but these are offset somewhat by a higher energy density in the liquid. Materials such as paper, which are high in cellulose content, give bio-oil yields in the range of 75 to 93% – yields in excess of 75 wt% are typical of a mixed paper stream.

The pyrolysis process results in the transformation of a solid or moist feedstock into a liquid, with conversion efficiency normally exceeding 50%. Considerable quantities of char and other waste products are also produced and must be disposed of. The chemical composition of pyrolysis oil is highly dependent upon the feedstock utilized, but the process itself inevitably results in a complex mixture of chemicals, primarily consisting of hydrocarbon derivatives, and sometimes totaling more than a hundred. Pyrolysis oil is characteristically fairly viscous, brown in color, unstable, and quite corrosive. Energy content varies, but is roughly on a par with that of the viscous high-boiling residual crude oil used for heating and for fueling large ships.

Bio-oil is typically a liquid, almost black through dark red-brown. The density of the liquid is approximately $1,200\text{ kg/m}^3$, which is higher than of fuel oil, and significantly higher than of the original biomass. The viscosity of the oil varies from as low as 25 cP up to 1,000 cP depending on the water content, and the original feedstock. Due to large amounts of oxygenated components present, bio-oil has a polar nature and does not mix readily with hydrocarbon derivatives. The degradation products from the biomass constituents include organic acids (like formic and acetic acid), giving the oil its low pH of approximately 2 to almost 4. Typically, bio-oil is a low-sulfur, non-viscous, renewable liquid fuel – it is an oxygenated and, as such, is not a hydrocarbon fossil fuel. The oil has a fuel value of least 7,500 BTU/lb, which is approximately the same as air-dried wood and is between the fuel value of methanol and crude oil-derived fuel oil. Bio-oil is a clean-burning fuel that can be fired in existing fossil fuel boilers with minimal modifications, although the tendency for any signs of incompatibility with crude oil-derived fuel oils should be investigated before blending.

Water is an integral part of the single-phase chemical solution. The (hydrophilic) bio-oils have water contents of typically 15-35 wt.%. Typically, phase separation does occur if the water content is higher than approximately 30 to 45%. The heating values: the higher heating value (HHV) is below 19 MJ/kg compared to 42-44 MJ/kg for conventional fuel oils.

A totally different process than that used for biodiesel production can be used to convert biomass into a type of fuel similar to diesel which is known as bio-oil. The process (*fast pyrolysis, flash pyrolysis*) occurs when solid fuels are heated at temperatures between 350 and 500°C (660 to 930°F) for a short period of time (<2 seconds). The bio-oils currently produced are suitable for use in boilers for electricity generation.

In another process, the feedstock is fed into a fluidized bed (at 450 to 500°C, 840 to 930°F) and the feedstock flashes and vaporizes. The resulting vapors pass into a cyclone where solid particles, char, are extracted. The gas from the cyclone enters a quench tower where it is quickly cooled by heat transfer using bio-oil already made in the process. The bio-oil condenses into a product receiver, and any non-condensable gases are returned to the reactor to maintain process heating. The entire reaction from injection to quenching takes only two seconds.

In the hydrothermal upgrading process (HTU process), biomass is treated with water at high temperature (300 to 350°C, 570 to 660°F) and pressure (1,770 to 2,650 psi) to produce bio-crude. This can be separated by flashing or extraction to heavy (high-density) crude oil (suitable for co-combustion in coal power stations) and light (low-density) crude oil, which can be upgraded by hydrodeoxygenation (HDO) to biofuels.

The *rapid thermal processing* process (RTP™ process) occurs at a temperature of approximately 500°C (930°F), when a turbulent stream of hot sand flashes the biomass into a vapor. The vapor is then rapidly condensed into a liquid. This process occurs in less than two seconds, yielding high quantities of bio-oil (typically 65 to 75% w/w yield of pyrolysis oil from dried lignocellulosic biomass).

Bio-oil is a dark brownish viscous liquid that bears some resemblance to fossil crude oil. However, bio-oil is a complex oxygenated compound comprised of water, water-soluble compounds, such as acids, esters, etc., and water-insoluble compounds, usually called pyrolytic lignin because it comes from the lignin fraction of the biomass. The elemental composition of bio-oil is similar to that of the parent biomass. Because of its high oxygen content, the heating value (Btu per gallon) of bio-oil is lower than fossil fuel, typically only approximately half the heating value of fossil crude such as high-boiling fuel oil. However, it contains less nitrogen and only traces of metals or sulfur.

Bio-oil is acidic with a pH in the 2-4 range, making it highly unstable and corrosive – the acidity can be lessened by the addition of readily available base compounds. It, therefore, presents transportation/piping and storage challenges including the tendency to corrode most metals. Hence, it is usually transported and stored in stainless steel containers.

Like other biofuels, the properties of bio-oil are variable and dependent on the feedstock. The specific gravity of the liquid is approximately 1.10 to 1.25, which means it is slightly heavier than water, heavier than fuel oil, and significantly heavier than the bulk density of the original biomass. The viscosity of the oil varies from as low as 25 cP up to 1,000 cP, depending on the water content and the original feedstock.

Processes are available to crack (thermally decompose) and hydrotreat pyrolysis oil to produce more familiar refined products such as diesel oil, kerosene, and gasoline, but the conversion efficiency and energy efficiency of such cracking is poor, and near or midterm commercialization seems unlikely. An alternative processing strategy is to gasify the pyrolysis oil to produce synthesis gas and then proceed with Fischer-Tropsch catalytic processing to produce a range of refined synfuels—this on the theory that most gasifiers are better able to cope with liquids than solids. The Carbo-V process is an example of a combined pyrolysis-gasification production technology for converting biomass into liquid fuels.

See also: Bio-oil, Carbo-V Process, Product Analysis, Pyrolysis, Pyrolysis Processes, Refining.

Quality

The term quality (as applied to a gas or liquid stream), is measured by the amount of energy that is obtained from burning a measured volume of the gas or liquid in British thermal units (Btu). The economic value of the gas stream is estimated from the Btu value insofar as the gas stream may have (i) a low Btu value, or (ii) a medium Btu value, or (iii) a high Btu value.

The composition of gas stream with the source from which the gas is produced. The different hydrocarbons that are contained within a gas stream can be separated using their different physical properties as weight, boiling point, or vapor pressure. Depending on its content of heavy components, the gas stream gas can be considered as rich (five or six gallons or more of recoverable hydrocarbons per cubic feet) or lean (less than one gallon of recoverable hydrocarbons per cubic feet).

The energy content of a gas stream is variable and depends on its accumulations, which are influenced by the amount and types of energy gases they contain: the more noncombustible gases in a gas stream, the lower the Btu value. In addition, the volume mass of energy gases that are present in a gas stream accumulation also influences the Btu value of gas stream. The more carbon atoms in a hydrocarbon gas, the higher its Btu value. Btu analyses of gas stream are done at each stage of the supply chain. Gas chromatographic process analyzers are used in order to conduct fractional analysis of the gas stream, separating gas stream into identifiable components. The components and their concentrations are converted into a gross heating value in British thermal units per cubic foot (Btu/ft³).

Typically, a gas stream – as it is when extracted from a process – is not suitable for pipeline transportation or commercial use before being processed. Pipelines set their specifications for the quality of gas stream. In any case, gas stream must be processed in order to remove unwanted water vapor, solids, or other contaminants and to get those hydrocarbons that have a higher value as separate products.

See also: High Btu Gas, Low-Btu Gas, Medium Btu Gas.

Quench

Quenching, rapid cooling, as by immersion in oil or water, of an object or process product from the high temperature at which it has been treated. Quenching can also be referred to as shock cooling as when a (relatively) cool liquid to the hot reactants. An example is the termination of the reactions by adding a quench liquid to the hot products as they merge from a thermal unit. The quench stream reduces the potential for further reaction of the hot visbreaker liquids.

Water quenching is a rapid cooling, where water as a quenching medium extracts heat much faster. While oil as a medium will extract heat much slower, hence the rate of cooling will be slower than water.

In chemistry, the term work-up refers to the series of manipulations (which may be considered to be quenching processes) that are required to isolate and purify the product(s) of a chemical reaction. Typically, these manipulations may include: (i) quenching a reaction to deactivate any unreacted reagents, (ii) cooling the reaction mixture or adding an antisolvent to induce precipitation and collecting or removing the solids by filtration, decantation, or centrifugation, (iii) removal of solvents by evaporation, (iv) separating the reaction mixture into organic and aqueous layers by liquid-liquid extraction, and (v) purification by chromatography, distillation, or recrystallization.

Thus, in an industrial process, quenching is the process of terminating a reaction by suddenly decreasing the temperature of the reactants, thereby reducing the potential for secondary reactions or tertiary reactions that could destroy the integrity and yield of the desired product(s).

In the quenching process (which can be air-quenching or liquid-quenching), the performance of heat transfer relates greatly on the characteristics of air flow or liquid flow, and these characteristics vary with the conditions of interfaces, in particular, the gradients of temperature. Because the conjugate heat transfer is transient, the characteristics of the process may vary with respect to time.

Radiation

Radiation is the emission or transmission of energy in the form of waves or particles through space or through a material medium. Radiation can be produced in one of two ways which are (i) by radioactive decay of an unstable atom (radionuclide), or (ii) by the interaction of a particle with matter. Some attributes of radioactive decay are that it is spontaneous and random, and the type of radiation emitted depends on the specific radionuclide.

Radiation is also often categorized as either ionizing or non-ionizing depending on the energy of the radiated particles. A common source of ionizing radiation is radioactive materials that emit α -radiation, β -radiation, or γ -radiation, consisting of helium nuclei or electrons or positrons, or photons, respectively. The term ionize refers to the breaking of one or more electrons away from an atom, an action that requires the relatively high energies that these electromagnetic waves supply. Further down the spectrum, the non-ionizing lower energies of the lower ultraviolet spectrum cannot ionize atoms, but can disrupt the inter-atomic bonds which form molecules, thereby breaking down molecules rather than atoms. The waves of longer wavelength than ultraviolet light in visible light, infrared, and microwave frequencies cannot break bonds but can cause vibrations in the bonds which are sensed as heat.

Radiation emission as the result of an interaction, on the other hand, depends on both the incoming particle and the material it hits, and is theoretically predictable if enough information is known. Radioactive decay and interactions will be discussed in more detail in the following sections. Radiation is described by its type and energy, and the types of radiation fall into two main categories: (i) particulate and (ii) electromagnetic. Particulate radiation consists of particles that have mass and energy, and may or may not have an electric charge.

On the other hand, electromagnetic radiation consists of photons that have energy, but no mass or charge. A photon (sometimes referred to as a packet of light), as described by quantum theory, is a particle or quantum that contains a discrete quantity of electromagnetic energy which travels at the speed of light, or 3×10^8 meters per second. Visible light, ultraviolet light, x-rays, and gamma rays are all photons.

See also: Radioactive Decay, Radioactivity.

Radiation – Types

There are several types of radiation present in nature and anthropogenic sources: (i) alpha particles, (ii) beta particles, (iii) gamma rays, (iv) x-rays, and (v) neutrons. A radioactive atom sooner or later will emit radiation in order to attain a more stable state. In some cases, it turns out that the daughter nucleus is also unstable – and consequently will emit another particle. Thus, there is a series of radioactive atoms of which uranium is the most common example. The starting point is the uranium-238 (^{238}U) isotope which decays through 14 steps and results in the production of the stable lead-206 isotope (^{206}Pb) (Table R-1).

Table R-1 The uranium-radium series.

Isotope	Radiation Type	Half-life
Uranium-238	Alpha	4.47 billion years
Thorium-234	Beta	24.21 days
Protoactinium-234	Beta	1.17 minutes
Uranium-234	Alpha	245,000 years
Thorium-230	Alpha	77,000 years
Radium-226	Alpha	1,600 years
Radon-222	Alpha	3.82 days
Polonium-218	Alpha	3.05 minutes
Lead-214	Beta	26.8 minutes
Bismuth-214	Beta	19.8 minutes
Polonium-214	Alpha	0.164 milliseconds
Lead-210	Beta	22.3 years
Bismuth-210	Beta	5.01 days
Polonium-210	Alpha	138.4 days
Lead 206	N/A	Stable

Radon (a noble gas) and the radon decay products (the 5 isotopes from radon-222 to and including polonium-214) have short half-lives.

Alpha Particles

Alpha particles are the slowest of the different types of radiation. They can travel only a few inches in the air, losing their energy almost as soon as they collide with anything. They can easily be shielded with a sheet of paper or the outer layer of a person's skin. An alpha particle has a large mass and two protons and no electrons. Because it has two protons and no electrons, it is positively charged. When emitted from the nucleus, the positive charge causes the alpha particle to strip electrons from nearby atoms as it passes.

An α -particle is the nucleus of helium. It has a charge of +2 and a weight of 4 atomic mass units. The “mother” nucleus (M) is changed into a “daughter” nucleus (D) according to the following reaction:



A is the atomic mass, i.e., the number of protons and neutrons, and Z is the atomic number, i.e., the number of protons.

The emitted alpha-particles all have the same energy, or are distributed in a few mono-energetic groups. The energy is high – ranging from 1.5 MeV to about 11 MeV. Almost all α -particle sources are found among the heavy elements, and most of them are natural. The daughter nucleus is very often unstable – and most often emits gamma radiation.

An alpha particle is identical in makeup to the nucleus of a helium atom, consisting of two neutrons and two protons. Alpha particles have a positive charge and have little or no penetrating power in matter. They are easily stopped by materials such as paper and have a range in air of only an inch or so. Naturally occurring radioactive elements such as uranium and radon daughters emit alpha radiation.

Alpha particles are extremely hazardous to fire fighters because they can be inhaled and deposited in body tissues, where they can cause severe long-term health effects. Positive pressure is effective protection against inhaling alpha particles. These agents can affect the cells of the body in various ways, and each is capable of destroying cells.

Alpha decay is the process in which an isotope releases a helium nucleus (2 protons and 2 neutrons) and thus decays into an atom with two less protons.



Beta Particles

Beta particles are more energetic than alpha particles and can travel in the air for a distance of a few feet. Beta particles can pass through a sheet of paper but may be stopped by a sheet of aluminum foil or glass. A beta particle has a small mass and is usually negatively charged. It is emitted from the nucleus of an atom with a charge of minus one. Beta radiation causes ionization by interfering with electrons in their orbits. Both have a negative charge, so the electrons are repelled when the beta particle passes.

An unstable nucleus may attain a more stable configuration by emitting a β -particle. In this process, a neutron in the nucleus is transformed into a proton and an electron (see illustration). Due to the difference in mass, a neutron is sometimes considered to be a proton + an electron + a small subatomic particle (the *neutrino*).

Both natural sources and artificial radioactive sources may be β -particle emitters. The energy of the emitted β -particle is usually much smaller than that of the α -particles. Furthermore, the energy of the β -particles varies from one disintegration to another! In fact, β -particle emission involves a whole spectrum of energies. The reason for this situation is that together with the β -particle, a tiny neutral particle (a neutrino) is emitted. Thus:

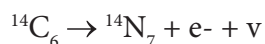


In this process, the mass A is unchanged and the proton number (Z) increases by one.

The kinetic energy of the β -particle and the neutrino combined is constant. The energy of the β -particle alone varies from zero up to a maximum value – equal to the constant. The average energy of the β -particle is on the order of 33% of this maximum energy.

Thus, beta radiation is composed of particles that are identical to electrons. As a result, beta particles have a negative charge. Beta radiation is slightly more penetrating than alpha but may be stopped by materials such as aluminum foil and panels composed of Lucite (an acrylic plastic resin). The particles have a range in air of several feet. Naturally occurring radioactive elements such as potassium-40 (^{40}K) emit beta radiation. Beta particles can damage the skin or tissues of the eye. Internally, they can be extremely damaging if they concentrate in specific tissues.

Beta decay is the process in which one of the neutrons in an isotope decays, leaving a proton, electron, and anti-neutrino. As a result, the nucleus decays into an atom that has the same number of nucleons, with one neutron replaced by a proton. Beta positive decay is the reverse process, in which a proton decays into a neutron, anti-electron, and neutrino.

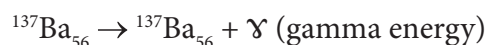


Gamma Rays

Gamma rays (unlike alpha or beta particles) are waves of pure energy; they have no mass. They are emitted from the nucleus of an atom and travel at the speed of light (186,000 miles per second). Gamma radiation can be very penetrating and requires concrete, lead, or steel to stop it.

Gamma radiation is a form of electromagnetic radiation, like radio waves or visible light, but with a much shorter wavelength. It is more penetrating than alpha or beta radiation, capable of passing through dense materials such as concrete. X-rays are similar to gamma radiation.

Gamma decay is the process in which an excited atomic nucleus kicks out a photon and releases some of its energy. The makeup of the nucleus doesn't change; it just loses energy.

*Neutron Particles*

Neutrons are particles normally contained in the nucleus of an atom. They can be released through certain manufacturing processes, such as nuclear fission (splitting an atomic nucleus).

Neutrons are considerably larger than beta particles but have only one-fourth the mass of an alpha particle. Because they can penetrate even thick lead shields, they can be extremely damaging to humans. However, neutron radiation is rare since it is generally emitted only when atomic weapons are detonated.

X-rays

X-rays are essentially the same as gamma rays except that they are emitted from the electrons that orbit the atom's nucleus, rather than from the nucleus itself. Gamma rays and X-rays are also called photons. Because they have high energy and penetrate deeply, gammas and X-rays can affect not only specific organs, but the surrounding tissues as well.

Gamma radiation and X-rays are electromagnetic waves or photons and have no electrical charge. The difference between the two is that gamma rays originate inside the nucleus and X-rays originate outside the nucleus. Both can ionize an atom by directly interacting with the electrons.

Radioactive Decay

Radionuclides are inorganic chemicals that emit radiation because their atoms are unstable and they disintegrate or decay as they release energy in the form of radioactive particles or waves. There are many different types of radioactive decay. A decay, or loss of energy from the nucleus, results when an atom with an initial type of nucleus (the parent radionuclide or parent radioisotope) transforms into a daughter nuclide. The transformation produces an atom in a different state (a nucleus containing a different number of protons and neutrons). In some decay processes, the parent and the daughter nuclides are different chemical elements, and thus the decay process results in the creation of an atom of a different element (nuclear transmutation). Another type of radioactive decay results in products that are not defined, but appear in a range of molecular fragments of the original nucleus (spontaneous fission) which occurs when a large unstable nucleus spontaneously splits into two (and occasionally three) smaller daughter nuclei, and generally leads to the emission of gamma rays, neutrons, or other particles from those products.

Unlike other inorganic elements or chemicals, radionuclides degrade naturally, but the degradation process itself is hazardous to living things. The risk posed by radionuclides is a function of the type and amount of radiation, as well as exposure pathways. The half-life (the time required to reduce the concentration of a chemical to 50% of the initial concentration) of a radioactive element (Table R-2). Moreover, the radioactive half-life for a given radioisotope is a measure of the tendency of the nucleus to decay (disintegrate) and is based upon that probability.

Table R-2 Examples of the half-life of several elements and isotopes.

Isotope	Half-life
Carbon-11	20.4 minutes
Carbon-12	5,730 years
Cesium-137	30.2 years
Cobalt-60	5.27 years
Iodine-123	13.2 hours
Iodine-131	8.05 days
Oxygen-15	2.02 minutes
Phosphorus-32	14.3 days
Potassium-40	1.3 billion years
Radon-222	3.82 days
Strontium-90	28.2 years
Sulfur-35	87.4 days
Thallium-201	3.04 days
Thorium-232	14 billion years
Tritium	12.3 years
Uranium-235	704 million years
Plutonium-239	24,100 years

The half-life is independent of the physical state (solid, liquid, gas), temperature, pressure, the chemical compound in which the nucleus exists, and essentially any other outside influence. The half-life is also independent of the chemistry of the atomic surface, and independent of the ordinary physical factors of the environment in which the chemical exists.

Radioactive Isotopes

Matter is composed of atoms whose nuclei contain protons and neutrons. Many elements which are found within the Earth system exist in different atomic configurations (isotopes) which have same atomic number but differ in their atomic mass. A radioactive isotope (also called a radioisotope, a radionuclide, or a radioactive nuclide) is any of several species of the same chemical element with different masses in which the nuclei are unstable and dissipate excess energy by spontaneously emitting radiation in the form of alpha, beta and gamma rays. These unstable elements decay by emission of energy; such isotopes, which emit radiation, are the radioactive isotopes (also referred to as radioisotopes).

The number of protons in the nuclei determines whether the atom is hydrogen, carbon, uranium, oxygen, or one of the other 115 currently known elements. For example, most carbon atoms will have 6 protons and 6 neutrons. Atoms of the same element, however, may have different numbers of neutrons in their nuclei. The various forms of an element that differ only in the number of neutrons are referred to as isotopes; one element may have many different isotopes. Some carbon atoms have five, seven, or eight neutrons. Since an isotope is identified by the element name and its atomic weight (i.e., the sum of the protons and neutrons in each atom), carbon atoms with six neutrons

in their nuclei (the dominant form) have an atomic weight of $6+6=12$ and are referred to as carbon-12. Carbon atoms with five, seven, or eight neutrons in their nuclei are referred to as carbon-11, carbon-13, and carbon-14, respectively. Isotopes of the same element generally have virtually identical chemical characteristics but may differ in other ways. For example carbon-12 is stable whereas carbon-14 is unstable, or radioactive. Stable isotopes maintain their nuclear structure without changing over time. Radioactive isotopes, referred to as radioisotopes or radionuclides, have unstable nuclei which spontaneously disintegrate and release energy in the process to form other nuclear particles that can be detected by a radioactivity-measuring instrument.

See also: Radiation, Radioactive Decay.

Radioactive Metals

The term radioactive metals refers to natural and synthetic metals that can release alpha (α), beta (β), and gamma (γ) rays. These metals fall into a group of radioactive elements (Table R-3), some of which can be put to usage in many ways for the benefit of human beings, such as power generation, nuclear battery, material engineering, and treatment of cancer.

Table R-3 List of radioactive elements*.

Element, symbol, atomic number	Most Stable Isotope	Half-life*
Technetium, Tc, 43	Tc-91	4.21×10^6 years
Promethium, Pm, 61	Pm-145	17.4 years
Polonium, Po, 84	Po-209	102 years
Astatine, At, 85	At-210	8.1 hours
Radon, Rn, 86	Rn-222	3.82 days
Francium, Fr, 87	Fr-223	22 minutes
Radium, Ra, 88	Ra-226	1600 years
Actinium, Ac, 89	Ac-227	21.77 years
Thorium, Th, 90	Th-229	7.54×10^4 years
Protoactinium, Pa, 91	Pa-231	3.28×10^4 years
Uranium, U, 92	U-236	2.34×10^7 years
Neptunium, Np, 93	Np-237	2.14×10^6 years
Plutonium, Pu, 94	Pu-244	8.00×10^7 years
Americium, Am, 95	Am-243	7370 years
Curium, Cm, 96	Cm-247	1.56×10^7 years
Berkelium, Bk, 97	Bk-247	1380 years
Californium, Cf, 98	Cf-251	898 years
Einsteinium, Es, 99	Es-252	471.7 days
Fermium, Fm, 100	Fm-257	100.5 days
Mendelevium, Md, 101	Md-258	51.5 days
Nobelium, No, 102	No-259	58 minutes

(Continued)

Table R-3 List of radioactive elements*. (Continued)

Element, symbol, atomic number	Most Stable Isotope	Half-life*
Lawrencium, Lr, 103	Lr-262	4 hours
Rutherfordium, Rf, 104	Rf-265	13 hours
Dubnium, Db, 105	Db-268	32 hours
Seaborgium, Sg, 106	Sg-271	2.4 minutes
Bohrium, Bh, 107	Bh-267	17 seconds
Hassium, Hs, 108	Hs-269	9.7 seconds
Meitnerium, Mt, 109	Mt-276	0.72 seconds
Darmstadtium, Ds, 110	Ds-281	11.1 seconds
Roentgenium, Rg, 111	Rg-281	26 seconds
Copernicium, Cn, 112	Cn-285	29 seconds
Nihonium, Nh, 113	Nh-284	0.48 seconds
Flerovium, Fl, 114	Fl-289	2.65 seconds
Moscovium, Mc, 115	Mc-289	87 milliseconds
Livermorium, Lv, 116	Lv-293	61 milliseconds
Tennessine, Ts, 117	Ts-294	51 milliseconds
Oganesson, Og, 118	Og-294	1.8 milliseconds

*Many of these elements (Americium to Oganesson, atomic numbers 95 to 118) are synthetic insofar as they do not occur naturally and have only been created in the laboratory.

Radioactivity is a natural part of the environment of the Earth which contains several primordial long-lived radioisotopes that have survived to the present in significant amounts. Potassium-40 (^{40}K), with a 1.3 billion-year half-life, has the lowest mass of these isotopes and beta decays to both argon-40 (^{40}Ar) and calcium-40 (^{40}Ca). Many isotopes can decay by more than one method. Three high atomic number elements: thorium-232 (^{232}Th , with a 14.1 billion year half-life), uranium-235 (^{235}U , with a 700 million year half-life), and uranium-238 (^{238}U , with a 4.5 billion year half-life) decay through emission of alpha and beta decays ending at the stable lead-208 (^{208}Pb), lead-207 (^{207}Pb), and lead-206 (^{206}Pb), respectively. The current ratio of uranium to lead present on Earth gives an estimate of the age of the Earth at 4.5 billion years (4.5×10^9 years). One of the intermediate products of the uranium-238 decay chain, radon-222 (^{222}Rn) with a half-life of 3.8 days, is responsible for higher levels of background radiation in many parts of the world – primarily because radon is a gas and can easily seep out of the earth into unfinished basements and then into the house. Some radioactive isotopes, for example carbon-14 (^{14}C) and beryllium-7 (^7Be), are produced continuously through reactions of cosmic rays (high-energy charged particles from outside the Earth) with molecules in the upper atmosphere.

Also, the study of radioactivity is important to understand the structure of the Earth because radioactive decay heats the interior of the Earth to high temperatures giving rise to geothermal heat and energy.

See also: Geothermal Energy.

Radioactive Waste

Radioactive waste is produced at all stages of the nuclear fuel cycle, from the initial mining of the uranium to the final disposal of the spent fuel from the reactor. The term *radioactive waste* encompasses a broad range of material with widely varying characteristics. Some radioactive waste is barely radioactive and safe to handle, whereas other

types are intensely hot and highly radioactive. For example, some radioactive wastes decay to safe levels of radioactivity in a matter of days or weeks, whereas other types will remain dangerous for thousands of years.

Disposal

Disposal is the final step in the management of radioactive waste. The aim is to provide safety through emplacement of waste in facilities designed for appropriate levels of containment and isolation. However, the proper disposal of radioactive waste is still highly challenging and is one of the most difficult kinds of waste to manage because of the hazardous nature of the waste and such waste is required to be very carefully stored or reprocessed.

In fact, with the continued interest in generating energy from alternative sources such as, in this context, nuclear sources, the challenge of making nuclear power safer does not end after the power has been generated. The nuclear fuel remains dangerously radioactive for thousands of years after it is no longer useful in a commercial reactor. The resulting waste disposal problem has become a major challenge for the industry.

Disposing radioactive waste is unquestionably one of the major problems associated with the development of nuclear power; radioactive waste is also a by-product of nuclear weapons plants, hospitals, and scientific research. Even though federal policy is based on the assumption that radioactive waste can be disposed of safely, new storage and disposal facilities for all types of radioactive waste have frequently been delayed or blocked by concerns about safety, health, and the environment.

The highly toxic wastes must be isolated from the environment until the radioactivity decays to a safe level. In the case of plutonium, for example, the half-life is twenty-six thousand years. At that rate, it will take at least one hundred thousand years before radioactive plutonium is no longer dangerous. Any facilities built to store such materials must last at least that long.

High-Level Waste

High-level radioactive wastes are the highly radioactive materials produced as a by-product of the reactions that occur inside nuclear reactors. High-level waste takes one of two forms: (i) spent (used) reactor fuel when it is accepted for disposal and (ii) waste material remaining after spent fuel is reprocessed.

Uranium fuel can be used for twelve to eighteen months, after which it is no longer as efficient in splitting its atoms and producing the heat needed to generate electricity. It must be removed from the reactor and replaced with fresh fuel. Some of the spent fuel is reprocessed to recover the usable uranium and plutonium, but the radioactive material that remains is dangerous for thousands of years.

Safe methods for the final disposal of high-level radioactive waste are technically proven; the international consensus is that geological disposal is the best option.

Low-Level Waste

Low-level waste, which contains lesser levels of radioactivity, includes trash (such as wiping rags, swabs, and syringes), contaminated clothing (such as shoe covers and protective gloves), and hardware (such as luminous dials, filters, and tools). This waste comes from nuclear reactors, industrial users, government users (but not nuclear weapon sites), research universities, and medical facilities. In general, low-level waste decays relatively quickly (in ten to one hundred years).

A somewhat lower-level (than high-level) hazardous type of radioactive waste is waste that has been exposed to alpha radiation, or that contains long-lived radionuclides in concentrations that require isolation and containment for periods beyond several hundred years, is classified as intermediate-level radioactive waste. This type of waste includes resins, chemical sludge, and metal nuclear fuel cladding, as well as contaminated materials from reactor decommissioning. For disposal, this type of waste may be solidified in concrete or bitumen or mixed with silica sand and vitrified, although this method is not without some risk and danger.

Typically, low- and intermediate-level radioactive wastes are buried in geological repositories. These repositories must isolate the nuclear waste from the biosphere for as long as 100,000 years. For the storage of radioactive waste, the geological formations were used where water-soluble compounds have been accumulated for millions of years, such as salt mines, clay rocks, granite, and tuff. In these geological formations, further engineering barriers are constructed. The nuclear waste is placed into stainless steel or reinforced concrete containers and deposited inside the engineering barrier system. Only solid wastes are stored; liquid wastes are solidified by cementation. The holes

among the containers are filled with cement too. In the geological repositories, there are several barrier systems (rocks, engineering barriers) which one by one must isolate the radioactive waste from the environment.

There are several aspects to take into account when selecting a suitable environment for waste disposal. These are, for example, (i) the hydrological properties of the geological environment, (ii) the potential corrosion and erosion of the engineering barrier system, (iii) leaching, and migration of the radionuclide in the geological environment. In addition, the microbiological activity and the effects of radiolysis must be considered.

In the corrosion and microbiological degradation of these substances, gaseous product may be released. The corrosion produces hydrogen, while the microbiological processes transform the organic substances of the nuclear wastes into carbon dioxide or methane, depending on the redox conditions. The gases can have unfavorable effects during storage. For example, the increasing pressure can push the radioactive gases and solutions into the environment. As a result of the cementation, the pH of the pore solution is set above 12 which inhibits the corrosion of the containers and the microbiological activity, decreasing the rate of gas release.

The leaching and migration of radionuclides is the overall effect of hydrological, interfacial (adsorption, ion exchange), and chemical processes (hydrolysis, precipitation, redox reactions). The interactions are determined by the surface charge of minerals and rocks, and the chemical species of the radioactive isotopes.

Mixed Waste

Mixed waste is high-level, low-level, or transuranic waste that also contains hazardous nonradioactive waste. Such waste poses serious institutional problems because of the radioactive portion. Such waste must be handled carefully and sent for disposal according to the laws and regulations of the necessary authorizes.

Transuranic Waste

Transuranic waste is a by-product of weapons production, nuclear research, and power production, and consists of protective gear, tools, residue, debris, and other items contaminated with small amounts of radioactive elements (mainly plutonium). Transuranic waste includes the eleven man-made radioactive elements with atomic numbers greater than that of uranium (ninety-two) and therefore beyond (*trans-*) uranium (*-uranic*) on the Periodic Table of the elements. The half-lives (the time it takes for half the radioisotopes present in a sample to decay to nonradioactive elements) of these elements are on the order of thousands of years.

Uranium Mill Tailings

Uranium mill tailings are primarily the sandy process waste material from a conventional uranium mill. This ore residue contains the radioactive decay products from the uranium chains (mainly the uranium-238, ^{238}U , chain) and heavy metals.

Even though the tailings may emit low levels of radiation, the large volume of the material poses a hazard, particularly from radon emissions and groundwater contamination. The dangers of uranium mill tailings were not realized until the early 1970s, so many miners and residents of the western United States were exposed to them. Cancer incidences are high among miners who worked before the 1970s.

See also: Periodic Table of the Elements.

Radioactivity

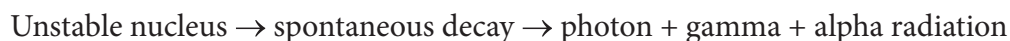
Radioactivity is the spontaneous emission of energy and/or high-energy particles from the nucleus of an atom. One type of radioactivity is produced naturally and is emitted by radioactive isotopes (or radioisotopes), such as radioactive carbon (carbon 14, or C-14) and radioactive hydrogen (H-3, or tritium). The energy and high-energy particles that radioactive isotopes emit include alpha rays, beta rays, and gamma rays.

In nature, the nuclei of most atoms are stable. However, certain atoms have unstable nuclei due to an excess of either protons or neutrons, or an excess of both. They are described as radioactive, and are known as radioisotopes or radionuclides.

The nuclei of radioactive atoms change spontaneously into other atomic nuclei, which may or may not be radioactive. For instance, uranium-238 (^{238}U) changes into a succession of different radioactive nuclei until it reaches a

stable form, lead-206 (^{206}Pb) (Table R-1). This irreversible transformation of a radioactive atom into a different type of atom is known as disintegration. It is accompanied by the emission of different types of radiation. A chemical element can therefore have both radioactive isotopes and non-radioactive isotopes. For example, carbon-12 is not radioactive, but carbon-14 is. Because radioactivity only affects the nucleus and not the electrons, the chemical properties of radioactive isotopes are the same as those of stable isotopes.

In radioactive processes, particles or electromagnetic radiation are emitted from the nucleus. A radioactive atom possesses an unstable nucleus. This means that radioactive atoms will emit radiation sooner or later and by this convert into a more stable state that can be represented simply as:



Thus, the most common forms of radiation that may be emitted are (i) alpha (α), (ii) beta (β), and gamma (γ) radiation.

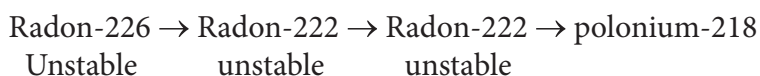
Nuclear radiation occurs in other forms, including the emission of protons or neutrons or spontaneous fission of a massive nucleus. Of the nuclei found on Earth, the vast majority is stable. This is so because almost all short-lived radioactive nuclei have decayed during the history of the Earth. There are approximately 270 stable isotopes and 50 naturally occurring radioisotopes (radioactive isotopes). Thousands of other radioisotopes have been made in the laboratory.

Radioactive decay will change one nucleus to another if the product nucleus has a greater nuclear binding energy than the initial decaying nucleus. The excess binding energy appears as kinetic energy or rest mass energy of the decay products. However, nuclear decay processes must satisfy several conservation laws, meaning that the value of the conserved quantity after the decay, taking into account all the decay products, must equal the same quantity evaluated for the nucleus before the decay.

The probability that a particular nucleus will undergo radioactive decay during a fixed length of time does not depend on the age of the nucleus or how it was created. Although the exact lifetime of one particular nucleus cannot be predicted, the mean (or average) lifetime of a sample containing many nuclei of the same isotope can be predicted and measured. A convenient way of determining the lifetime of an isotope is to measure how long it takes for one-half of the nuclei in a sample to decay—this quantity is called the half-life, $t_{1/2}$. Of the original nuclei that did not decay, half will decay after another half-life, leaving one-quarter of the original sample after a total time of two half-lives. After three half-lives, one-eighth of the original sample will remain and so on. Measured half-lives vary from tiny fractions of seconds to billions of years, depending on the isotope.

In the process of alpha decay, the nucleus emits a ^4He nucleus, an alpha particle. Alpha decay occurs most often in massive nuclei that have too large a proton-to-neutron ratio. An alpha particle, with its two protons and two neutrons, is a very stable configuration of particles. Alpha radiation reduces the ratio of protons to neutrons in the parent nucleus, bringing it to a more stable configuration. Nuclei, which are more massive than lead, frequently decay by this method.

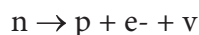
As an example, Radium (atomic number 88) has an unstable nucleus weighing 226 atomic units. It decays by emitting an α -particle and becomes a new element radon (^{222}Rn , atomic number 86). Radon-226 is however unstable and will in turn decay into polonium (^{218}Po).



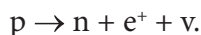
Thus, in alpha decay, the atomic number changes, so the original (or parent) atoms and the decay-product (or daughter) atoms are different elements and therefore have different chemical properties. In the alpha decay of a nucleus, the change in binding energy appears as the kinetic energy of the alpha particle and the daughter nucleus.

Because this energy must be shared between these two particles, and because the alpha particle and daughter nucleus must have equal and opposite momenta, the emitted alpha particle and recoiling nucleus will each have a well-defined energy after the decay. Because of the smaller mass, most of the kinetic energy goes to the alpha particle.

Beta decay occurs when, in a nucleus with too many protons or too many neutrons, one of the protons or neutrons is transformed into the other. In beta-minus decay, a neutron decays into a proton, an electron, and an antineutrino:



In beta plus decay, a proton decays into a neutron, a positron, and a neutrino:



Both reactions occur because one or the other will move the product closer to the region of stability. These particular reactions take place because conservation laws are obeyed. Electric charge conservation requires that if an electrically neutral neutron becomes a positively charged proton, an electrically negative particle (in this case, an electron) must also be produced. Similarly, conservation of lepton number requires that if a neutron (lepton number = 0) decays into a proton (lepton number = 0) and an electron (lepton number = 1), a particle with a lepton number of -1 (in this case an antineutrino) must also be produced. The leptons emitted in beta decay did not exist in the nucleus before the decay—they are created at the instant of the decay.

An isolated proton (i.e., a hydrogen nucleus with or without an electron) does not decay. However, within a nucleus, the beta decay process can change a proton to a neutron. An isolated neutron is unstable and will decay with a half-life of 10.5 minutes. A neutron in a nucleus will decay if a more stable nucleus results; the half-life of the decay depends on the isotope. If it leads to a more stable nucleus, a proton in a nucleus may capture an electron from the atom (electron capture), and change into a neutron and a neutrino.

Proton decay, neutron decay, and electron capture are three ways in which protons can be changed into neutrons or vice-versa; in each decay, there is a change in the atomic number, so that the parent and daughter atoms are different elements. In all three processes, the number A of nucleons remains the same, while both proton number, Z, and neutron number, N, increase or decrease by 1. In beta decay, the change in binding energy appears as the mass energy and kinetic energy of the beta particle, the energy of the neutrino, and the kinetic energy of the recoiling daughter nucleus. The energy of an emitted beta particle from a particular decay can take on a range of values because the energy can be shared in many ways among the three particles while still obeying energy and momentum conservation.

In gamma decay, a nucleus changes from a higher energy state to a lower energy state through the emission of electromagnetic radiation (photons). The number of protons (and neutrons) in the nucleus does not change in this process, so the parent and daughter atoms are the same chemical element. In the gamma decay of a nucleus, the emitted photon and recoiling nucleus each have a well-defined energy after the decay. The characteristic energy is divided between only two particles.

The units of radioactivity relate to the number of decays per second, or activity, from a sample of radioactive nuclei is measured in becquerel (Bq, named after Henri Becquerel), and one decay per second equals one becquerel. An older unit is the curie (named after Pierre and Marie Curie), and one curie is approximately the activity of 1 gram of radium and equals (exactly) 3.7×10^{10} becquerel. The activity depends only on the number of decays per second, not on the type of decay, the energy of the decay products, or the biological effects of the radiation.

See also: Radioactive Decay.

Radionuclides

A radionuclide (also called radioactive nuclide, radioisotope, or radioactive isotope) is an unstable atom because of excess nuclear energy. This excess energy can be used in one of three ways: (i) emitted from the nucleus as gamma radiation, (ii) transferred to one of the electrons to release it as a converted electron, or (iii) used to create and emit new particles, such as an alpha particle or a beta particle from the nucleus. These emissions are sufficiently powerful

to liberate an electron from another atom. The radioactive decay can produce a stable nuclide or will sometimes produce a new unstable radionuclide which may undergo further decay.

Because of the unstable nucleus, a radionuclide is a radioactive element that is typically referred to by a name followed by a number, for example cesium-137 (Cs-137 or ^{137}Cs ; Cs is the chemical symbol for cesium as it appears in the Periodic Table of the Elements). The number following the name of the element is the mass of the element and is equal to the total number of particles contained in the nucleus of the atom.

Exposure to radionuclides generally has a harmful effect on living organisms including humans, although low levels of exposure occur naturally without harm. The degree of harm will depend on the nature and extent of the radiation produced, the amount and nature of exposure (close contact, inhalation, or ingestion), and the biochemical properties of the element, with increased risk of cancer as the most usual consequence. However, radionuclides with suitable properties are used in nuclear medicine for both diagnosis and treatment.

See also: Radioactivity.

Rankine Cycle

The Rankine cycle is the thermodynamic cycle for the steam turbine and is the basis for conventional power-generating stations and consists of a heat source (boiler) that converts water to high-pressure steam.

In the steam cycle, water is first pumped to elevated pressure, which is medium-to- high pressure, depending on the size of the unit and the temperature to which the steam is eventually heated. It is then heated to the boiling temperature corresponding to the pressure, boiled (heated from liquid to vapor), and then most frequently superheated (heated to a temperature above that of boiling). The pressurized steam is expanded to lower pressure in a turbine, then exhausted either to a condenser at vacuum conditions, or into an intermediate temperature steam distribution system that delivers the steam to the industrial or commercial application. The condensate from the condenser or from the industrial steam utilization system is returned to the feedwater pump for continuation of the cycle.

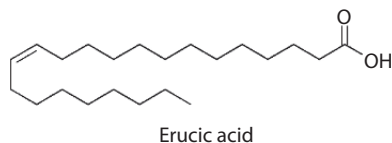
Thus, there are four processes in the Rankine cycle which are (i) a process in which the working fluid is pumped from low to high pressure; as the fluid is a liquid at this stage, the pump requires little input energy, also known as the isentropic compression process, (ii) a process in which the high-pressure liquid enters a boiler, where it is heated at constant pressure by an external heat source to become a dry saturated vapor; in this segment of the cycle, also known as constant pressure heat addition in boiler, (iii) a process in which the dry saturated vapor expands through a turbine thereby generating power – this decreases the temperature and pressure of the vapor, and some condensation may occur; this is also known as isentropic expansion, and (iv) a process in which the wet vapor enters a condenser where it is condensed at a constant pressure to become a saturated liquid – also known as constant pressure heat rejection in condenser.

In an ideal Rankine cycle, the pump and turbine would be isentropic insofar as the pump and turbine would generate no entropy and hence maximize the net-work output. However, the actual vapor power cycle may differ from the ideal Rankine cycle because of irreversibility in the inherent components caused by fluid friction and heat loss to the surroundings – fluid friction causes pressure drops in the boiler, the condenser, and the piping between the components, and as a result, the steam leaves the boiler at a lower pressure while heat loss reduces the net-work output and, as a result, heat addition to the steam in the boiler is required to maintain the same level of net-work output.

Rapeseed

Rapeseed (*Brassica napus*), also known as rape oil, oilseed rape, and, in the case of one particular group of cultivars, canola, is a bright-yellow flowering member of the family Brassicaceae (mustard or cabbage family), cultivated mainly for its oil-rich seed. It is the third-largest source of vegetable oil and second-largest source of protein meal in the world. There are two subspecies: (i) *Brassica napus* ssp. *Napobrassica*, also known as the swedes rape and (ii) *Brassica napus* ssp. *Napus* which includes the winter and spring oilseed, vegetable, and fodder rape forms. The *pabularia* variety (Siberian kale) is a distinct leaf rape form of the *napus* subspecies which used to be common as a winter-annual vegetable. Rapeseed can be cultivated on a wide variety of well-drained soils, preferably at a pH between 5.5 and 8.3, and has a moderate tolerance of soil salinity.

Rapeseed oil is one of the oldest known vegetable oils, but historically was used in limited quantities due to high levels of erucic acid, which is damaging to cardiac muscle of animals, and glucosinolate derivatives, which made it less nutritious in animal feed. Rapeseed oil can contain up to 54% w/w erucic acid.



Rapeseed oil is used as diesel fuel, either as biodiesel, straight in heated fuel systems, or blended with crude oil distillates for powering motor vehicles. Biodiesel may be used in pure form in newer engines without engine damage and is frequently combined with crude oil-derived diesel in ratios varying from 2% to 20% v/v biodiesel. Owing to the costs of growing, crushing, and refining rapeseed biodiesel, rapeseed-derived biodiesel from new oil costs more to produce than standard diesel fuel, so diesel fuels are commonly made from the used oil. Rapeseed oil is the preferred oil stock for biodiesel production in most of Europe, accounting for approximately 80% v/v of the feedstock, partly because rapeseed produces more oil per unit of land area compared to other oil sources, such as soybeans, but primarily because canola oil has a significantly lower gel point than most other vegetable oils.

In agriculture, canola is a variety of rapeseed oil, or the oil produced from those varieties. Canola is a trademark for a hybrid variety of rape initially bred in Canada. Rapeseed oil was produced in the 19th century as a source of a lubricant for steam engines, and the oil has a bitter taste due to high levels of acids. Canola has been bred to reduce the amount of acid, yielding a more palatable oil.

Rapeseed oil is used in the manufacture of biodiesel for powering motor vehicles. Biodiesel may be used in pure form in newer engines without engine damage, and is frequently combined with fossil-fuel diesel in ratios varying from 2% to 20% biodiesel. Formerly, owing to the costs of growing, crushing, and refining rapeseed biodiesel, rapeseed-derived biodiesel costs more to produce than standard diesel fuel. Rapeseed oil is the preferred oil stock for biodiesel production in most of Europe, partly because rapeseed produces more oil per unit of land area compared to other oil sources, such as soy beans.

There is, however, concern over the use of rapeseed for use as biodiesel because rapeseed is currently grown with a high level of nitrogen-containing fertilizers and the manufacture of these generates nitrous oxide (N_2O), a potent greenhouse gas with 296 times the global warming potential of carbon dioxide. It has been estimated that 3 to 5% of nitrogen provided as fertilizer for rapeseed is converted to nitrous oxide.

See also: Biodiesel, Biomass – Extraction.

Rapeseed Methyl Ester

Rapeseed methyl ester is a methyl ester of natural fatty acids (predominantly the C18 fatty acid). The product is an excellent solvent with good biodegradability and toxicity properties (benign toxicity in case of ingestion or contact).

The methyl esters of rapeseed oil are important alternative diesel fuels based on renewable sources. A discontinuous plant production of the methyl esters involves a two-stage low-temperature transesterification of cold-pressed rapeseed oil with methanol at temperatures up to 70°C (158°F). The total methanol-acyl molar ratio of 4:3, with an optimum distribution of methanol between the two stages and a 4% sodium hydroxide in methanol as the catalyst. The final treatment of methyl ester with phosphoric acid and ammonia provides for an exchange of ashy soap forms in the ester for ashless forms, thus rendering the methyl ester as a non-corrosive product.

See also: Biomass – Extraction, Rapeseed.

Rate of Reaction

The rate of reaction is the rate at which the moles or mass of reactants are depleted or products formed with respect to time per unit volume (or per unit weight or surface of catalyst in case of solid-catalyzed reactions) of the reactor. Thus:

$$r_A = (1/V)(dN_A/dt) = dC_A/dt$$

N_A is the moles of A in the reactor at any time, t is the time in seconds, and V is the volume of the reactor. From concentration of reactant A data taken for different reaction time, the rate can be evaluated from the above relation. The rate is also conveniently expressed as a function of C_A :

$$r_A = kC_A^n$$

in this equation, n is the order of reaction and may be any value positive or negative integer that is specific for the reaction which may be first order ($n = 1$), second order ($n = 2$), third order ($n = 3$), and even fractional order; many reactions also manifest a more complicated reaction order, especially the multiple or reversible reactions.

Reactor Types

Chemical reactors (reactors, reactor vessels) are used widely in the various energy oriented industries to purify feedstocks and convert feedstocks into products. This is naturally facilitated by chemical reactions. The choicer of the reactor is dictated by the nature of the reaction and the reaction parameters – high pressure or low pressure, high temperature or low temperature. The classification of the reactor type is mainly based on the number of phases present in the reactor since the character of reactive phases to a large extent decides the physical configuration of reactor equipment (Table R-4).

Furthermore, homogeneous or homogeneously catalyzed reactions can be facilitated in a simple tube or tank reactors, but for heterogeneous catalytic reactions, the reactor typically has a solid catalyst phase, which is not consumed as the reaction takes place. Thus, heterogeneous catalytic reactions are commonly carried out in packed bed reactors, in which the reacting gas or liquid flows through a catalyst bed.

Table R-4 Various reactor-types.

<i>Homogeneous reactors</i> Only one phase (gas or liquid); homogeneous catalyst Examples: tube reactor (plug flow reactor), tank reactor (stirred tank reactor, CSTR), batch reactor, semi-batch reactor.
<i>Heterogeneous catalytic two-phase reactors</i> Two phases: one fluid phase; gas or liquid phase; solid catalyst; reaction takes place on the catalyst surface Examples: packed bed, moving bed, fluidized bed.
<i>Heterogeneous catalytic three-phase reactors</i> Three phases: gas, liquid, and solid catalyst; reaction takes place on the catalyst surface
<i>Gas-liquid reactors</i> A gas phase and a liquid phase; homogenous catalyst; reaction takes place in the liquid phase Examples: absorption column, bubble column, tank reactor, reactive distillation column monolith reactors
<i>Liquid-liquid reactors</i> Two liquid phases; homogeneous catalyst; reaction can take place in both phases Examples: column reactor, mixer-settler reactor.
<i>Fluid-solid reactors</i> Two or three phases; one fluid phase (gas/liquid); one reactive solid phase; reaction between the solid phase and the gas/liquid phase Examples: packed bed, fluidized bed

Fixed bed or slurry bed reactors are the two conventional reactor types currently used for processes. Fixed bed reactors are comparable to the shell and tube heat exchangers that are common in the process industries. In these,

the catalyst, in the form of cylindrical pellets, is contained within 2.5–5 cm (1–2 inch) tubes that are oriented vertically within a large vessel. In the latest fixed bed reactors (for the Fischer-Tropsch process, as an example), these tubes are 1 inch in diameter and approximately 40 feet tall. The biggest challenge with conventional fixed bed reactors lies in controlling the temperature within the reactor tubes. Since some processes (such as the Fischer-Tropsch process) are exothermic and strongly affected by temperature, a hot spot can develop within the center of the tube, resulting in a substantial drop in the catalyst performance. As a result, the performance of fixed bed reactors is limited by heat transfer.

In slurry bed reactors, the catalysts take the form of small particulates (on the order of 50 microns in diameter; 1 micron = $1 \text{ mm} \times 10^{-3} = 1 \text{ meter} \times 10^{-6}$) that are suspended in the liquid wax produced by the reaction. The heat generated by the reaction is removed by coolant tubes that run throughout the reactor.

A micro channel reactor is a reactor that consists of numerous channels with small diameters of less than a few millimeters, and microchannel process technology is used in a range of applications. These include the large number of chemical and process systems that involve thermal processing, ranging from ethane cracking to fuel processing catalytic processes, such as hydrocracking; chemical reactions and production, for example, steam methane reforming and ethylene oxidation; separations, mixing, and emulsification; catalytic processes; gas processing for operations such as hydrogen production; biological and medical applications; and integrated and multi-phase systems. In terms of small-scale distributed biomass-to-liquids production, microchannel reactors offer particular advantages.

For example, because the structure and dynamics of microchannel reactors improves heat transfer between process fluids and channel walls, the biomass-to-liquids process is intensified. In addition, microchannel reactors also allow the use of more active catalysts than conventional systems, which greatly increases the throughput per unit volume of the reactors. The use of microchannel process technology offers a number of advantages in a range of energy and chemical processing applications. These include: (i) improved heat transfer properties and (ii) higher energy efficiency. Microchannel has thin reaction channels which greatly improves heat and mass transfer. This allows optimal temperature control across the catalyst bed, which maximizes catalyst activity and life.

See also: Fischer-Tropsch Process.

Reburning

Reburning is an effective and economic means of reducing NO_x emissions from all types of industrial and electric utility boilers.

Reburning, or the staged introduction of fuel into a combustion device, is based on laboratory-scale studies in the early 1970s. The first commercial-scale application of this technology to control NO_x emissions was installed in Japan during the same decade. Subsequently, commercial-scale testing was conducted in the U.S. and Europe, mainly on electric utility boilers, but also to some extent on municipal waste incinerators.

Reburning involves the staged addition of fuel into two combustion zones which are (i) the primary combustion zone where coal is fired, and (ii) the reburn zone where additional fuel (the reburn fuel) is added to create a reducing (oxygen-deficient) condition to convert the NO_x produced in the primary zone to molecular nitrogen and water. Above the reburn zone is a burnout zone in which overfire air is added to complete the combustion.

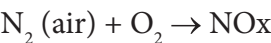
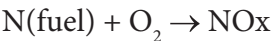
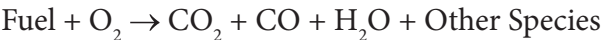
Each zone has a unique stoichiometric air ratio (the ratio of the air used to that theoretically required for complete combustion) as determined by the flows of primary fuel, burner air, reburn fuel, and overfire air.

Coal is fired under normal-to-low excess air conditions at a rate corresponding to 70–90% of the total heat input. The amount of NO_x created in this zone is reduced by approximately 10% because less coal is fired (lower production of fuel NO_x), the heat release rate is lower (lower production of thermal NO_x), and, generally, the excess air level to the burners is reduced (a lower oxygen concentration results in lower emissions of nitrogen oxide(s)).

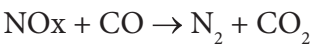
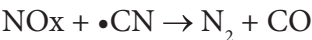
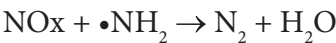
Reburn fuel injection creates a reducing region within which the reburn fuel molecules break down to hydrocarbon fragments (CH , CH_2 , etc.) that react with NO_x , producing reduced nitrogen species (mainly N_2). The optimum reburn zone stoichiometric ratio is 0.85 to 0.95. This is achieved by injecting reburn fuel at a rate corresponding to 10–30% of the total heat input, depending on the primary zone excess air level. The lower the primary combustion zone excess air, the lower the reburn fuel requirement.

In the burnout zone, overfire air is injected downstream of the reburn zone to complete combustion. Overfire air is typically 20% v/v of the total air flow with an overall excess air level of 15 to 25% being usual. The *overfire air* injection rate is optimized for each specific application to minimize carbon monoxide emissions and unburned carbon in the fly ash. Thermal NO_x formation in the burnout zone is small because of the lower temperature. Depending on the nature of the reburn fuel used, various boiler retrofits are required. The following equations represent the general chemistry of the process:

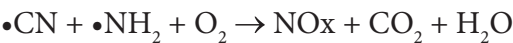
Primary Combustion Zone (Low to normal excess air; stoichiometric ratio of 1.1-1.2) –



Reburn Zone (Fuel-rich; stoichiometric ratio of 0.85-0.95) –



Burnout Zone (Normal excess air; stoichiometric ratio of 1.20-1.25) –



See also: Combustion.

Recoverable Reserves

Recoverable reserves (Table R-5) are that portion of resource reserves that are economically and technically feasible to extract at the existing price of the resource commodity.

Table R-5 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Non-recoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Recoverable reserves fluctuate with the price of the commodity. Resources are considered recoverable reserves if they can be developed with reasonable certainty from a given date under current economic conditions, operating methods, and government regulations.

Resource reserves have specific classifications related to the degree of certainty with which they can be recovered, based on seismic and engineering data. Degrees of uncertainty are expressed by dividing oil reserves into two primary classifications, proven and unproven.

See also: Reserves.

Recovery Boiler

A recovery boiler is a pulp mill boiler in which lignin and spent cooking liquor (black liquor) are burned to generate steam. A recovery boiler is the part of Kraft process of pulping where chemicals for white liquor are recovered and reformed from black liquor, which contains lignin from previously processed wood.

Concentrated black liquor contains organic dissolved wood residue in addition to sodium sulfate from the cooking chemicals added at the digester, and combustion of the organic portion of chemicals produces heat. In the recovery boiler, heat is used to produce high-pressure steam, which is used to generate electricity in a turbine. The turbine exhaust, low-pressure steam is used for process heating.

Combustion of black liquor in the recovery boiler furnace needs to be controlled carefully. The high concentration of sulfur requires optimum process conditions to avoid production of sulfur dioxide and reduced sulfur gas emissions. In addition to environmentally clean combustion, reduction of inorganic sulfur must be achieved in the char bed.

See also: Black Liquor, Combustion, Kraft Process.

Recovery Processes

An important aspect of energy generation (as waste product disposal) from any source is the application of the appropriate recovery process.

Recovery Processes Applicable to Gas Streams

The contaminants in waste gas streams can be gases, liquids, or solids and must be removed from the gas stream prior to discharge to the atmosphere if they provide a hazard to human health or the environment or if their loss represents major financial burden, as with some valuable materials. Typical examples of hazardous gases are toxic materials such as carbon monoxide, hydrogen sulfide, and hydrogen cyanide, as well as environmentally undesirable gases such as oxides of nitrogen and sulfur and vapors from hazardous liquids such as paint solvents, gasoline, and halogenated cleaning solvents. The liquids in gases are all in the form of mists or fogs either caused by entrainment from gas-liquid contacting or by condensation of vapors in the gas stream due to cooling. Finally, the solids are usually in the form of dusts entrained in the gas stream.

Recovery of Gases from Gas Streams

The separation of homogeneous gas mixtures requires either some way of generating a second equilibrium phase or a technique which takes advantage of differing rates of reaction or of mass transport of the components of the gas mixture. At the present time, the techniques most frequently used in waste minimization depend on generation of a second phase, although membrane processes that depend on relative mass transport rates may become of increasing importance in gas recycling operations in the future.

The common ways of generating the second phase are (i) the use of a solid sorbent such as activated carbon, or (ii) the use of a liquid solvent selective for the undesirable contaminant (Table R-6).

Table R-6 Processes for the recovery of gases from gas streams.

Process	Description
Absorption	Absorption, stripping, and scrubbing
Adsorption	Adsorption, ion exchange, reversible reaction with solids
Chemical reaction	Adsorption, ion exchange, reversible reaction with solids
Permeation	Membrane processes
Scrubbing	Absorption, stripping, and scrubbing

These materials can work either by physical or chemical interaction with the contaminants. For example, solid adsorbents can attract an adsorbed phase merely by the physical nature of its surface structure or by building into the adsorbent a chemical functionality which reacts with specific materials in the gas phase to sequester them. Similarly, the addition of a solvent can lead to a physical separation process or a chemical one. For example, in absorption and scrubbing with liquid solvents, the solvent can either provide a liquid phase to permit separation of the gas mixture by physical distillation, or can actually react chemically with one or more of the contaminants in the feed gas to bind them chemically into the solvent phase. Both types of adsorbents and solvents are in common use.

Recovery of Liquids from Gas Streams

As mentioned above, the liquids found in gases are usually in the form of mists or fogs and can be removed effectively by mechanical means. The basic problem with mists and fogs is to coalesce the tiny liquid droplets into larger drops that can be more readily removed from the gas phase by settling. This can be done by the addition of ultrasonic energy to the gas phase, by passing the gas phase through a cyclone to centrifuge out the liquid, by impacting the droplets on a solid surface such as metal mesh demisters and coalescers, or by contacting the droplets with a liquid surface such as exists in scrubbers and absorbers (Table R-7).

Table R-7 Processes for the recovery of liquids from gas streams.

Process	Description
Absorption	Absorption, stripping, and scrubbing
Coalescence	Settling and flotation
Condensation	Distillation
Cyclones	Centrifuging and cycloning
Electrostatics	Electrostatic preoccupation, electrochemical processes
Filtration	Filtration and drying
Scrubbing	Absorption, stripping, and scrubbing

Recovery of Solids from Gas Streams

The entrainment of solids in gases is in the form of fine particles classed as dusts. Since they form a second phase, as with liquids in gases, they are also separated by mechanical techniques. Large particles can be readily settled out of a gas phase, but dust-like particles generally require some form of mechanical help. This mechanical help can take the form of cyclones, filters, scrubbers, or electrostatic precipitators, and all are in common use (Table R-8).

Table R-8 Processes for the recovery of solids from gas streams.

Process	Description
Cyclones	Centrifuging and cycloning
Electrostatics	Electrostatic preoccupation, electrochemical processes
Filtration	Filtration and drying
Scrubbing	Absorption, stripping, and scrubbing

Recovery Processes Applicable to Liquid Streams

The contaminants in liquid streams may also be either gases, liquids, or solids. Furthermore, the liquid streams may be either homogeneous or heterogeneous, depending on whether the contaminants are in solution or form a second phase. The gases are easily settled out by gravity unless they are dissolved, of small bubble size, or the liquid is extremely viscous. Heterogeneous liquid phases often exist as clouds of very tiny droplets in a continuous phase of a second liquid. These systems can be difficult to separate by mechanical means, especially if the densities of the droplets and of the continuous phase are close to each other. Finally, solid contaminants can also be either dissolved in a liquid phase or exist as a slurry of solid particles in the liquid carrier. The optimum separation process for recovery of each of these contaminants depends on the exact nature of the contaminated liquid. Recovery of the three different phases of contaminant is discussed below.

Recovery of Gases from Liquid Streams

When gases exist as a separate phase in liquids, they can usually be recovered by coalescing the entrained gas bubbles into large bubbles and letting them settle out of the liquid phase. If necessary, the viscosity of the continuous liquid phase can be reduced by heating to improve both coalescing and settling. On the other hand, if the gases are dissolved in the liquid phase, some sort of carrier phase must be generated to strip the dissolved gases out of the liquid. This can be an inert gas, such as steam, air, carbon dioxide, or nitrogen, blown through the liquid phase as a stripping gas in a stripping column. Alternatively, vapors generated from the liquid by heating it to a boil as in flash distillation can be used to strip out gases. In this latter case, the stripping gases are the vapors generated by the boiling liquid.

Recovery of Liquids from Liquid Streams

As with gaseous contaminants, liquid contaminants can also exist in liquid systems as either a separate liquid phase or as a homogeneous solution. When a heterogeneous system is encountered, the recovery processes are mechanical in nature such as settling, flotation, coalescing, cycloning, and centrifuging. On the other hand, if the system is homogeneous, either equilibrium- or rate-controlled processes must be used. The equilibrium processes are distillation, stripping, adsorption, extraction and supercritical extraction, ion exchange, and solvent precipitation. Finally, the rate-controlled processes are membrane diffusion and electrolytic processes (Table R-9).

Table R-9 Processes for the recovery of liquids from liquid streams.

Process	Description
Adsorption	Adsorption, ion exchange, reversible reaction with solids
Centrifuging	Centrifuging and cycloning
Cyclones	Centrifuging and cycloning
Distillation	Thermal fractionation
Extraction	Solvent extraction, solvent precipitation, and leaching
Flotation	Flotation and settling
Ion exchange	Adsorption, ion exchange, reversible reaction with solids

(Continued)

Table R-9 Processes for the recovery of liquids from liquid streams. (*Continued*)

Process	Description
Permeation	Membrane processes
Settling	Flotation and settling
Solvent precipitation	Solvent extraction, solvent precipitation, and leaching
Stripping	Adsorption, stripping, and scrubbing
Reverse osmosis	Membrane processes
Ultrafiltration	Membrane processes

Recovery of Solids from Liquid Streams

Solid contaminants can also exist in liquids either as slurries or in the dissolved state. As with other heterogeneous systems, the slurries are separated by mechanical techniques such as settling, filtration, flocculation, flotation, centrifuging, and drying. With the homogeneous systems, evaporation and crystallization are frequently used to generate a heterogeneous system followed by one of the techniques for heterogeneous systems (Table R-10).

Table R-10 Processes for the recovery of solids from liquid streams.

Process	Description
Centrifuging	Centrifuging and cycloning
Chemical precipitation	Chemical precipitation and sedimentation
Crystallization	Evaporation and crystallization
Cyclones	Centrifuging and cycloning
Drying	Filtration and drying
Evaporation	Evaporation and crystallization
Filtration	Filtration and drying
Flocculation	Chemical precipitation and sedimentation
Flotation	Flotation and settling
Microfiltration	Membrane processes
Settling	Flotation and settling
Ultrafiltration	Membrane processes

Recovery Processes From Solid Streams

Solids can be contaminated with relatively small amounts of adsorbed gases liquids as with spent adsorbents, or with larger amounts of liquids as with cakes and sludges. Furthermore, solids can absorb either liquids or gases give swollen solids and gels. Solid polymers can show this latter behavior, and solids can exist as mixtures with other solids as in the case of many domestic and industrial solid wastes. All of these systems are discussed below.

Recovery of Gases from Solid Streams

Adsorbed gases can be recovered from solids by stripping the solids with a sensible gas such as steam. This permits the adsorbed gas to be recovered condensing the steam out of it. Alternatively, if the adsorbed gas is readily condensable, as with some vapors, fixed gases such as air, nitrogen, or carbon dioxide can be used for stripping. The desorbed vapors are recovered from the stripping gas by condensing them out of the stripping gas stream.

Dissolved gases require that the structure of the solid be changed to discharge the dissolved gases. This can frequently be done by raising the temperature of the solid during stripping to raise the partial pressure of the dissolved gases.

Recovery of Liquids from Solid Streams

Adsorbed liquids on solids can be recovered by stripping with immiscible condensable gases in much the same way as adsorbed gases (Table 3.6). However, they can also be washed off the solids with suitable solvents and then recovered from the resulting mixture with the solvent. Dissolved liquids may be recovered by heating the solids in a dryer under a stream of stripping gas.

Recovery of Solids from Solid Streams

Mixtures of solids use much different processes for separation from those used with liquids and gases. The usual separation processes are based on differences in density, particle size, surface properties, magnetic susceptibility, or electrostatic characteristics of the various solids (Table R-11).

Table R-11 Processes for the recovery of liquids from solid streams.

Process	Description
Centrifuging	Centrifuging and cycloning
Cyclones	Centrifuging and cycloning
Drying	Filtration and drying
Evaporation	Evaporation and crystallization
Extraction	Solvent extraction, solvent precipitation, and leaching
Filtration	Filtration and drying
Stripping	Absorption, stripping, and scrubbing

For example, with elutriation, in which a stream of gas is passed through a fluidized bed of solids of differing particle sizes and particle densities, the gas carries out with it the lightest and smallest particles first and can be used to make either a density separation or a particle size separation (Table R-12).

Table R-12 Processes for the recovery of solids from solid streams.

Process	Description
Electromagnetic	Separation of solids
Electrostatic	Separation of solids
Elutriation	Flotation and settling
Flotation	Flotation and settling
Screening	Separation of solids
Sorting	Separation of solids

Surface properties can be used to make a separation as with froth flotation in which dispersed air is bubbled through a slurry of a solid mixture in water and attaches bubbles of air to the solid particles selectively according to the surface properties of the individual solid particles. This makes the particles with the attached bubbles buoyant and carries them to the surface from which they can be recovered. The process is commonly used on a large scale in the mining industry to separate ores. Finally, electrostatic and magnetic separations of solids are frequently done on a moving belt which sorts materials according to their magnetic properties or their ability to accept an electrostatic charge (Table 3.7).

Process Selection

There are several general rules of thumb for decreasing energy consumption in separation processes. These rules of thumb were primarily aimed at process design, but they also give some insights into choosing processes and process equipment (Table R-13).

Table R-13 General rules for process selection.

1. Perform the mechanical separations first if more than one phase exists in the feed.
2. Avoid overdesign and use designs giving efficient turndown. Favor simple processes.
3. Favor processes transferring the minor rather than major component between phases,
3. Favor high separation factors.
4. Recognize value differences of energy in different forms and of heat and cold at different temperature levels,
6. Investigate use of heat pump, vapor compression, or multi-effects for separations with small temperature ranges.
7. Use staging or countercurrent flow where appropriate.
8. For similar separation factors, favor energy-driven processes over mass-separating agent processes.
9. For energy-driven processes, favor those with lower latent heat of phase change.

Mechanical separations such as settling, screening, filtration, centrifugation, flocculation, etc., are much less energy intensive than separation processes for homogeneous mixtures. Therefore, it is usually preferred to perform the separation of heterogeneous phases such as sludges and emulsions first before attacking the homogeneous mixtures. The removal of heterogeneous phases greatly simplifies the separation of homogeneous mixtures.

Most of the separation processes encountered in hazardous waste minimization are fairly simple, such as batch distillation, adsorption, settling, filtration, and the like. These have good turndown ratios, i.e., they can operate efficiently over a wide range of operating rates. It is important to have this capability, particularly for continuous processes such as wastewater treating and stack gas scrubbing where flow rates change in response to manufacturing operations.

Processes with high separation factors are important in making separation processes economical. It applies to many of the separations involved in waste minimization. For very dilute systems, there is a great advantage to using processes like ion exchange and adsorption for the impurity rather than evaporation of the water. Furthermore, for extraction type processes, it is better to extract the minor component rather than the major component to minimize solvent circulation and regeneration.

High separation factors greatly reduce the number of stages and thus the capital costs required for a separation (Rule 4). They can frequently be increased to essentially infinity by adding a specific reagent that only reacts with one component of the feed mixture. Examples of processes having high separation factors are ion exchange for demineralizing water, chemical complexing for mixtures of olefins and paraffins, adsorption of aromatics from mixtures with saturated hydrocarbons, and to a lesser extent adding a selective solvent to a distillation to convert it to an extractive distillation. Many waste streams, such as solvents in motor oils, have a naturally high separation factor for distillation due to the large difference in boiling point between the homogeneous feed components. These solvents can be recovered in satisfactory purity for recycling in single-stage batch stills, and many such operations are already in place.

Heat and refrigeration energy are inherently less expensive than electrical energy or mechanical work. However, as the temperature at which the heat or refrigeration is used departs from ambient temperature, the cost of heat and refrigeration increases and these effects should be considered in choosing a separation process for a given feed mixture.

While mechanical work is more expensive than heat or refrigeration, it can sometimes permit latent heat of condensation to be exchanged for latent heat of vaporization. In such a case, which usually requires a small temperature

difference between the heat source and heat sink, vapor compression by mechanical work on the distillate can give it an increased pressure and condensing temperature, actually higher than the temperature in the boiler. This pumping of heat from a lower to a higher temperature permits the vapor to be condensed in the boiler generating the vapor in the first place. A balance between compressor cost and heat cost can determine the desirability of such operation. Staging and countercurrent flow can decrease the amount of separating agent needed and increase the purity of the products.

Energy-driven processes are inherently more efficient because they are more nearly reversible. They have the additional advantage that the energy can be readily removed by exchange with another stream and recycled to the process. This can be used to cascade the energy through a series of separations at gradually reducing temperature from initial source to final sink, using it over and over, thus minimizing the required supply of energy. To do the same type of thing with a mass separating agent requires an additional separation process for each exchange or recovery of the mass separating agent, thereby requiring much more energy.

Finally, in energy-driven processes, the energy is largely required to overcome the latent heat of phase change. Other things being equal, this favors heats of fusion over heats of vaporization and choice of selective solvents having lower heats of phase change in their recovery process. The use of multi-effect temperature cascades in the separation process can reduce the advantage offered by using low latent heat processes. While these rules of thumb are helpful in preliminary choices of separation processes, it must be remembered that the optimum separation process involves a balance between energy costs and the costs for equipment to minimize energy costs. Therefore, sometimes, it is desirable to pay for more energy and with the additional capital costs and operating complexity necessary to achieve high thermal efficiency.

Rectisol Process

The Rectisol process is a physical solvent gas treating process. The process uses chilled methanol (methyl alcohol, CH_3OH) at a temperature of approximately -40°F to -80°F . The selectivity (by methanol) for hydrogen sulfide over carbon dioxide at these temperatures is approximately 6/1, a little lower than that of the Selexol process at its usual operating temperature. However, the solubility of hydrogen sulfide and carbonyl sulfide in methanol, at typical process operating temperatures, is higher than in Selexol and allows for very deep sulfur removal. The high selectivity for hydrogen sulfide over carbon dioxide, combined with the ability to remove carbonyl sulfide, is the primary advantage of the process. The need to refrigerate the solvent is the main disadvantage of the process, resulting in high capital and operating costs. There are many possible process configurations for the Rectisol process, depending on process requirements. Different process layouts are used for selective hydrogen sulfide removal, and carbon dioxide, and for non-selective carbon dioxide and hydrogen sulfide.

The process is designed for the bulk removal of carbon dioxide, and nearly all of the removal of hydrogen sulfide and carbonyl sulfide takes place in the bottom section of the absorber. The methanol solvent contacting the feed gas in the first stage of the absorber is stripped in two stages of flashing via pressure reduction. The regenerated solvent is virtually free of sulfur compounds but contains some carbon dioxide. The acid gas leaving the first-stage solvent regenerator is suitable for a Claus plant. The second stage of absorption is designed for the removal of the remaining sulfur compounds and carbon dioxide. The solvent from the bottom of the second stage of the absorber is stripped deeply in a steam-heated regenerator and is returned to the top of the absorption column after cooling and refrigeration.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Redox Processes

A redox reaction is a type of chemical reaction in which the oxidation states of atoms are changed. Redox reactions are characterized by the actual or formal transfer of electrons between molecules. Thus, a redox process denotes a process in which there is a coupled reduction reaction and oxidation reaction, i.e., an electron transfer reaction where reduction is the uptake of electrons and oxidation is the release of electrons.

As an example of a redox process, liquid redox sulfur recovery processes are liquid-phase oxidation processes which use a dilute aqueous solution of iron or vanadium to remove hydrogen sulfide selectively by chemical absorption from sour gas streams. These processes can be used on relatively small or dilute hydrogen sulfide stream to recover sulfur from the acid gas stream, or, in some cases, they can be used in place of an acid gas removal process. The mildly alkaline lean liquid scrubs the hydrogen sulfide from the inlet gas stream, and the catalyst oxidizes the hydrogen sulfide to elemental sulfur. The reduced catalyst is regenerated by contact with air in the oxidizer(s). Sulfur is removed from the solution by flotation or settling, depending on the process.

See also: Claus Process, Gas Cleaning, Gas Processing, Gas Treating.

Reed Canary Grass

Reed canary grass is a robust perennial grass, widely distributed across temperate regions of Europe, Asia, and also North America. It occurs in wet places, along the margins of rivers, streams, lakes, and pools. The species spreads naturally by creeping rhizomes, but plants can also be raised from seed. The advantages of Reed Canary grass as an energy crop are its good adaptation to cool temperate climates and poor wet soil conditions and, conversely, its ability to withstand drought. Crucially, for the purposes of biomass production, reed canary grass is also able to attain high dry matter content earlier than *Miscanthus*. The crop responds well to nitrogen and phosphate, and it may be used in a bed system to remove nutrients from wastewater, as well as to stabilize areas at risk of soil erosion.

This rhizomatous grass can grow up to six feet in height and usually flowers in June and July. Reed canary grass is usually harvested once per year either by mowing or baling using a high-density baler. Crop duration of 10 years or more may be possible. Due to its low moisture content, canary grass (those harvested in spring) can be easily converted to pellets, briquettes, and powder.

The advantages of reed canary grass as an energy crop are its good adaptation to cool temperate climates and poor wet soil conditions and, conversely, its ability to withstand drought. Crucially, for the purposes of biomass production, reed canary grass is also able to attain high dry matter content earlier than *Miscanthus*. The crop responds well to nitrogen and phosphate, and it may be used in a bed system to remove nutrients from wastewater, as well as to stabilize areas at risk of soil erosion.

See also: Energy Crops, *Miscanthus*, Reed Plants, Short Rotation Coppice.

Reed Plants

Reed is a common name for several tall, grass-like plants that are commonly found in wetlands. Reed plants are a potentially prolific producer of biomass, capable of yielding 20 to 25 tons per hectare (2.47 acres) of dry matter annually for a number of years. They can grow up to 6 m, are spread by means of stout rhizomes (continuously growing horizontal underground stems, which puts out lateral shoots and adventitious roots at intervals) and stolons (also known as runners, which are horizontal connections between organisms), and are commonly found in swampy ground and shallow water throughout temperate and subtropical areas.

Common reeds grow well in damp ground or standing water, with stems up to 12 feet in height. It prefers full sun but can stand some partial shade. It requires an alkaline or neutral pH condition, not surviving in acidity. Wetland areas will see much reed bed growths. The leaves are an interesting color of blue green and are sharp to the touch. The flowers are small, usually only an inch wide, but the reed is commonly grown more for its foliage during the seasons for the blooms on it.

Reed plants may contain high amounts of heavy metals, and the heavy metals content appears to be inversely related to the sediment clay and/or organic matter content. Metal mobility and thus plant availability are higher in sediments with lower clay or organic matter content or a high salinity. Moreover, the plants might actively accumulate in particular essential elements when concentrations in the sediments are rather low, which is the case in sediments low in clay and organic matter contents.

On the other hand, reed plants have other uses such as phytoremediation, which is the use of plants and their associated microorganisms, to remove, contain, or degrade chemical contaminants from the environment. It is an

emerging technology for environmental remediation that offers promise as a low-cost, flexible technique suitable for use against a number of different types of contaminants in a variety of media. This illustrates the applicability of using reed plants in removing pollutants from contaminated water.

See also: Energy Crops, Reed Canary Grass.

Refinery Gas

The terms *refinery gas* and *petroleum gas* are often used to identify liquefied petroleum gas or even gas that emanates as light ends (gases and volatile liquids) from the atmospheric distillation unit or from any one of several other refinery processes.

For the purpose of this text, refinery gas not only describes liquefied petroleum gas but also natural gas and refinery gas. However, the composition of each gas varies and recognition of this is essential before the relevant testing protocols are selected and applied. Thus, refinery gas (fuel gas) is the non-condensable gas that is obtained during distillation of crude oil or treatment (cracking, thermal decomposition) of petroleum.

Refinery gas is produced in considerable quantities during the different refining processes and is used as fuel for the refinery itself and as an important feedstock for the production of petrochemicals. It consists mainly of hydrogen (H_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and olefins ($RCH=CHR^1$, where R and R^1 can be hydrogen or a methyl group) and may also include off-gases from petrochemical processes (Table 3.9). Olefins such as ethylene ($CH_2=CH_2$, boiling point: $-104^\circ C$, $-155^\circ F$), propene (propylene, $CH_3CH=CH_2$, boiling point: $-47^\circ C$, $-53^\circ F$), butene (butene-1, $CH_3CH_2CH=CH_2$, boiling point: $-5^\circ C$, $23^\circ F$), *iso*-butylene ($(CH_3)_2C=CH_2$, $-6^\circ C$, $21^\circ F$), *cis*- and *trans*-butene-2 ($CH_3CH=CHCH_3$, boiling point: ca. $1^\circ C$, $30^\circ F$), and butadiene ($CH_2=CHCH=CH_2$, boiling point: $-4^\circ C$, $24^\circ F$) as well as higher-boiling olefins are produced by various refining processes.

Still gas is broad terminology for low-boiling hydrocarbon mixtures and is the lowest boiling fraction isolated from a distillation (*still*) unit in the refinery. If the distillation unit is separating light hydrocarbon fractions, the still gas will be almost entirely methane with only traces of ethane (CH_3CH_3) and ethylene ($CH_2=CH_2$). If the distillation unit is handling higher-boiling fractions, the still gas might also contain propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$), and their respective isomers. *Fuel gas* and still gas are terms that are often used interchangeably, but the term *fuel gas* is intended to denote the product's destination – to be used as a fuel for boilers, furnaces, or heaters.

A group of refining operations that contributes to gas production are the thermal cracking and catalytic cracking processes. The thermal cracking processes (such as the coking processes) produce a variety of gases, some of which may contain olefin derivatives ($>C=C<$). In the visbreaking process, fuel oil is passed through externally fired tubes and undergoes liquid-phase cracking reactions, which result in the formation of lower-boiling fuel oil components. Substantial quantities of both gas and carbon are also formed in coking (both fluid coking and delayed coking) in addition to the middle distillate and naphtha. When coking a residual fuel oil or heavy gas oil, the feedstock is preheated and contacted with hot carbon (coke) which causes extensive cracking of the feedstock constituents of higher molecular weight to produce lower-molecular-weight products ranging from methane, via liquefied petroleum gas(es) and naphtha, to gas oil and heating oil. Products from coking processes tend to be unsaturated, and olefin-type components predominate in the tail gases from coking processes.

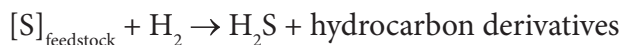
The various catalytic cracking processes, in which higher-boiling gas oil fractions are converted into gaseous products, various naphtha fractions, fuel oil, and coke by contacting the feedstock with the hot catalyst. Thus, both catalytic and thermal cracking processes, the latter being now largely used to produce chemical raw materials, result in the formation of unsaturated hydrocarbon derivatives, particularly ethylene ($CH_2=CH_2$), but also propylene (propene, $CH_3CH=CH_2$), isobutylene [isobutene, $(CH_3)_2C=CH_2$], and the *n*-butenes ($CH_3CH_2CH=CH_2$, and $CH_3CH=CHCH_3$) in addition to hydrogen (H_2), methane (CH_4), and smaller quantities of ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), and butane isomers [$CH_3CH_2CH_2CH_3$, $(CH_3)_3CH$]. Diolefins such as butadiene ($CH_2=CHCH=CH_2$) are also present.

In a series of reforming processes, distillation fractions which include paraffin derivatives, and naphthene derivatives (cyclic non-aromatic) are treated in the presence of hydrogen and a catalyst to produce lower-molecular-weight products or are isomerized to more highly branched hydrocarbon derivatives. Also, the catalytic reforming process

not only results in the formation of a liquid product of higher octane number but also produce substantial quantities of gaseous products. The composition of these gases varies in accordance with process severity and the properties of the feedstock. The gaseous products are not only rich in hydrogen but also contain hydrocarbon derivatives from methane to butane derivatives, with a preponderance of propane ($\text{CH}_3\text{CH}_2\text{CH}_3$), n-butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$), and isobutane [$(\text{CH}_3)_3\text{CH}$]. Since all catalytic reforming processes require substantial recycling of a hydrogen stream, it is normal to separate reformer gas into a propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) and/or a butane [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3/(\text{CH}_3)_3\text{CH}$] stream, which becomes part of the refinery liquefied petroleum gas production, and a lower-boiling gaseous fraction, part of which is recycled.

A further source of refinery gas is produced by the hydrocracking process which is a high-pressure pyrolysis process carried out in the presence of fresh and recycled hydrogen. The feedstock is again heavy gas oil or residual fuel oil, and the process is mainly directed at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again must be separated into lighter and heavier streams; any surplus recycle gas and the liquefied petroleum gas from the hydrocracking process are both saturated.

Both hydrocracker and catalytic reformer tail gases are commonly used in catalytic desulfurization processes. In the latter, feedstocks ranging from light to vacuum gas oils are passed at pressures on the order of 500 to 1,000 psi with hydrogen over a hydrofining catalyst. This results mainly in the conversion of organic sulfur compounds to hydrogen sulfide:



The process also has the potential to produce lower-boiling hydrocarbon derivatives by hydrocracking.

Refinery gas, usually in more than one stream, is typically treated for hydrogen sulfide removal, and gas sales are usually on a thermal content (calorific value, heating value) basis with some adjustment for variation in the calorific value and hydrocarbon type.

See also: Refining.

Refinery Waste

In spite of a refinery being a site for the conversion of fossil fuels (natural gas and crude oil) into valuable products, a refinery also produces a variety of waste material that can also be converted into useful products. For this reason, a refinery can be considered to be a source of energy from alternate sources.

Crude oil refining is the physical, thermal, and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished crude oil products. The primary products of the industry fall into three major categories which are (i) fuels, such as motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke, (ii) finished non-fuel products, such as solvents, lubricating oils, greases, crude oil wax, crude oil jelly, asphalt, and coke, and (iii) chemical industry feedstocks, such as ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene, and naphtha. These crude oil products are used as primary input to a vast number of products, including fertilizers, pesticides, paints, waxes, thinners, solvents, cleaning fluids, detergents, refrigerants, antifreeze, resins, sealants, insulations, latex, rubber compounds, hard plastics, plastic sheeting, plastic foam, and synthetic fibers.

The chemicals in crude oil vary from simple hydrocarbons of low-to-medium molecular weight to higher-molecular-weight organic compounds containing sulfur, oxygen, and nitrogen, as well as compounds containing metallic constituents, particularly vanadium nickel, iron, and copper. Many of these latter compounds are of indeterminate molecular weight. Residua contain significantly less hydrocarbon constituents than the original crude oil. The constituents of residua may, depending on the crude oil, be molecular entities of which the majority contains at least one heteroatom.

Typical refinery products include (i) natural gas and liquefied petroleum oil gas (LPG), (ii) solvent naphtha, (iii) kerosene, (iv) diesel fuel, (v) jet fuel, (vi) lubricating oil, (vii) various fuel oils, (viii) wax, (ix) residua, and

(x) asphalt. A single refinery does not necessarily produce all of these products. Some refineries are dedicated to particular products, e.g., the production of gasoline or the production of lubricating oil or the production of asphalt. However, the issue is that refineries also produce a variety of waste products that must be disposed in an environmentally acceptable manner.

Waste treatment processes also account for a significant area of the refinery, particularly sulfur compounds in gaseous emissions together with various solid and liquid extracts and wastes generated during the refining process. The refinery is therefore composed of a complex system of stills, cracking units, processing and blending units, and vessels in which the various reactions take place, as well as packaging units for products for immediate distribution to the retailer, e.g., lubricating oils. Bulk storage tanks usually grouped together in tank farms are used for storage of both crude and refined products. Other tanks are used in the processes outlined, e.g. treating, blending, and mixing, while others are used for spill and fire control systems. A boiler and electrical generating system usually operate for the refinery as a whole.

There are several hundred individual hydrocarbon chemicals defined as crude oil-based. Furthermore, each crude oil product has its own mix of constituents because crude oil varies in composition from one reservoir to another, and this variation may be reflected in the finished product(s).

Crude oil hydrocarbons are environmental contaminants, but they are not usually classified as hazardous wastes. Soil and groundwater crude oil hydrocarbon contamination has long been of concern and has spurred various analytical and site remediation developments, e.g., risk-based corrective actions. In some instances, it may appear that such clean-up operations were initiated with an incomplete knowledge of the character and behavior of the contaminants. The most appropriate first assumption is that the spilled constituents are toxic to the ecosystem. The second issue is an investigation of the products of the spilled material to determine an appropriate clean-up method. The third issue is whether or not the chemical nature of the constituents has changed during the time since the material was released into the environment. If it has, a determination must be made of the effect of any such changes on the potential clean-up method.

Despite the large number of hydrocarbons found in crude oil products and the widespread nature of crude oil use and contamination, many of the lower boiling constituents are well characterized in terms of physical properties, but only a relatively small number of the compounds are well characterized for toxicity. The health effects of some fractions can be well characterized based on their components or representative compounds (e.g., a low-boiling aromatic fraction benzene-toluene-ethylbenzene-xylenes). However, higher-molecular-weight (higher-boiling) fractions have far fewer well-characterized compounds.

See also Refining.

Refining

Crude oil refining is the separation of petroleum into fractions and the subsequent treating of these fractions to yield marketable products. In fact, a refinery is essentially a group of manufacturing plants which vary in number with the variety of products produced. Refinery processes must be selected and products manufactured to give a balanced operation in which petroleum is converted into a variety of products in amounts that are in accord with the demand for each. For example, the manufacture of products from the lower-boiling portion of petroleum automatically produces a certain amount of higher-boiling components. If the latter cannot be sold as, say, heavy fuel oil, these products will accumulate until refinery storage facilities are full. To prevent the occurrence of such a situation, the refinery must be flexible and be able to change operations as needed. This usually means more processes: thermal processes to change an excess of heavy fuel oil into more gasoline with coke as the residual product, or a vacuum distillation process to separate the heavy oil into lubricating oil blend stocks and asphalt.

The primary products of refining fall into three major categories: fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke). Non-fuel products (such as solvents, lubricating oils, greases, wax, asphalt, and coke) and chemical industry feedstocks (such naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene) are also produced.

See also: Refinery Waste.

Refining – Fischer-Tropsch Products

See also: Fischer-Tropsch Process – Product Separation and Upgrading

Refuse-Derived Fuel

Refuse-derived fuel (RDF) is fuel prepared from municipal solid waste after which any noncombustible materials such as rocks, glass, and metals are removed, leaving the remaining combustible portion of the solid waste chopped or shredded. Because of the potential for the inclusion of hazardous materials, the fuel is often categorized accordingly (Table R-14).

Table R-14 General categories of refuse-derived fuel.

Category	Common name	Description
RDF-1		Municipal solid wastes (MSW) used as a fuel in the discarded form
RDF-2	Coarse Fluff RDF	MSW processed to coarse particle size with or without ferrous material
RDF-3	Fine Fluff RDF	Shredded fuel derived from MSW that has been processed
RDF-4	Powdered RDF	Combustible waste processed into powdered form
RDF-5	Densified RDF	Combustible waste densified (compressed) into the form of pellets
RDF-6		Combustible waste processed into liquid fuel
RDF-7		Combustible waste processed into gaseous fuel

This is a result of processing municipal solid waste, facilitating recycling, re-use, and ensuring the homogenous nature of the waste. The non-combustible elements of the waste are left over after processing, giving the waste a higher calorific value. The new improved composition of the waste allows increased efficiency from incineration and reduced emissions and products as the waste that creates the harmful effects can be removed during processing.

The types of materials to be processed are the various combustible components, and such components include non-recyclable plastics, paper cardboard, labels, and generally corrugative materials. Because RDF can process such a variety of materials, there are different techniques to ensure the creation of a homogenous material that can be used as a substitute fossil fuel and act as a reduction agent in steel furnaces. The most common way of extracting refuse-derived fuel from municipal solid waste is to combine mechanical and biological treatment methods which include: (i) size screening, (ii) coarse shredding, (iii) bag splitting, (iv) shredding, (v) magnetic separation, and (vi) refining separation. Thus, the processing involves (i) separating unwanted components (for example by magnetically extracting ferrous metals), (ii) shredding, (iii) drying, and compacting the material into pellets. This type of processing allows fuel resources to become easily transported and more hygienically handled; it also allows incineration to play a part in waste management where reduction, reuse, and recycling can be maximized.

Further processing has also been developed; the end product is called densified refuse-derived fuel (d-RDF). This is a process by which the combustible part of the waste is separated, pulverized, compressed, and dried to produce solid fuel pellets that are approximately two inches long.

Refuse-derived fuel processes typically begin with shredding municipal solid waste to a finer size; many then separate the fuel fraction from the residue. In plants where no additional preparation is included, the operation is called a shred-and-burn refuse-derived fuel facility. Frequently, however, the separated fuel fraction is further processed to recover metals and sometimes glass. The normal sequence of refuse-derived fuel facility preparation is shredding, air classifying/screening, magnetic separation, and sometimes eddy current separation for nonferrous metal recovery. Many variations of the process have been developed, each of which has certain advantages.

Refuse-derived fuel is a useful feedstock for pyrolysis, gasification, and combustion since it grants a reasonably high heating value, suitable-sized particle size, and (in some cases) a more constant and homogeneous composition.

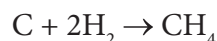
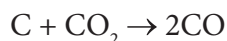
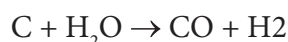
However, any differences in composition and the thermal degradation behavior make the process design, and operation of energy recovery units a challenge. Different waste require different treatments from pyrolysis to combustion, from fluffy material in fluidized bed to pellets, or briquettes in grate reactors. Thus, together with the combustion of different waste, the pyrolysis of waste tires to produce valuable oil, char, and gas products is of growing interest. Again, the most common reactors used are fixed-bed, screw and rotary kiln, vacuum, and fluid bed.

See also: Municipal Solid Waste, Scrap Tires, Waste.

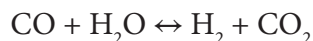
Refuse Gas

There are two ways of producing gaseous fuel from refuse or waste: (i) gasification of the refuse at high temperatures by partial oxidation and then conversion of materials containing carbon into synthesis gas (mainly hydrogen and carbon monoxide) and (ii) production of biogas, mainly methane, by the anaerobic digestion of the refuse in a landfill.

The principle behind waste gasification and the production of gaseous fuels is that waste contains carbon and it is this carbon that is converted to gaseous products via the usual gasification chemistry. This, when fuel is fed to a gasifier, water and volatile matter are released fast and a char residue is left to react further. The char gasification is what mainly controls the conversion achieved in the process. From solid carbon, product gas is formed according to the following main reactions:



In addition to the reactions of solid carbon, the most important reaction is the water-gas shift reaction, which takes place in the gas phase:



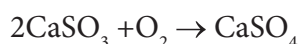
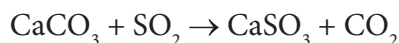
The product gas generally contains large amounts of hydrogen and carbon monoxide and a small amount of methane, as well as carbon dioxide and steam, and in air gasification nitrogen. In addition, a significant amount of other organic components in the gas, known as tar, is formed. Tar formation is a well-known phenomenon in the thermal reactions of coal and can also be anticipated to form in the gasification or pyrolysis of any complex carbonaceous material.

See also: Energy Production from Waste, Fuels from Waste, Gaseous Fuels from Waste, Refuse-Derived Fuel.

Regenerative and Non-Regenerative Gas Cleaning Processes

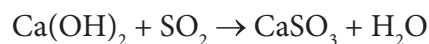
The procedures for the removal of sulfur dioxide can be classified further as regenerative or non-regenerative, depending upon whether the chemical used to remove the sulfur dioxide can be regenerated and used again or whether the chemical is unusable and passes to disposal.

In the wet regenerative processes, either elemental sulfur or sulfuric acid is recovered. In the wet non-regenerative processes, using lime and/or limestone, calcium sulfite or calcium sulfate sludge is produced that is disposed. Wet scrubbing processes contact the flue gas with a solution or slurry for sulfur dioxide removal. In a wet limestone process, the flue gas contacts a limestone slurry in a scrubber:



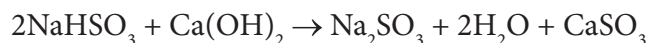
Both the sulfite and the sulfate absorb water of hydration to form a sludge composed of sulfite and sulfate derivatives.

In a wet lime process, a gas stream containing the sulfur dioxide is reacted with a wet lime slurry to form the sulfite:



There is subsequent conversion, by oxidation, to the sulfate.

In the double alkali non-regenerative procedure, flue gas is scrubbed with a soluble alkali such as sodium sulfite which is subsequently regenerated with lime to form insoluble calcium sulfite:



After this, disposal of the calcium sulfite slurry occurs and the spent absorbent, sodium bisulfite, is regenerated by thermal means:



In all of these procedures, water exits the system as vapor in the flue gas.

In either the lime/limestone or sodium sulfite/lime scrubbing processes, the hydrated calcium sulfite and calcium sulfate can be of some environmental concern when the issue of disposal arises. This has, more than anything else, promoted efforts to develop alternate dry scrubbing procedures for the removal of sulfur dioxide. The dry systems have the additional advantage of reducing the pumping requirements that are necessary for the wet systems.

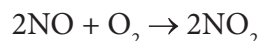
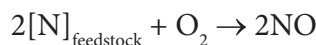
The tendency to advocate the use of dry lime scrubbing systems thereby produces a waste stream that can be handled by conventional fly ash removal procedures. There are also dry processes, such as the metal oxide processes, in which sulfur dioxide can be removed from gas streams by reaction with a metal oxide. These processes, which are able to operate at high temperatures (approximately 400°C; 750°F), are suitable for hot gas desulfurization without a cooling step. The metal oxides can usually be regenerated by aerial oxidation, to convert any metal sulfide(s) back to the oxide(s) or by use of a mixture of hydrogen and steam.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Removal of Nitrogen-Containing Gases

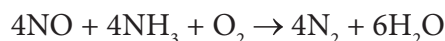
The occurrence of nitrogen in natural gas can be a major issue if the quantity is sufficient to lower the heating value. Several plants for the removal of nitrogen from the natural gas have been built, but it must be recognized that nitrogen removal requires liquefaction and fractionation of the entire gas stream which may affect process economics. In many cases, the nitrogen-containing natural gas is blended with a gas having a higher heating value and sold at a reduced price depending upon the thermal value (Btu/ft³).

Of equal interest is the occurrence of nitrogen compounds in gases produced by feedstock combustion. These compounds, the oxides, originate from the organically bound nitrogen in the coal:



Nitrogen oxides are formed during burning by oxidation, at the high temperatures, of the nitrogen in the fuel and in the air, giving rise to the terminology *thermal NOx* and *fuel NOx* as a means of distinguishing between the two sources of nitrogen oxides. Nitrogen oxides from whatever the sources are pollutants that must be removed from gas streams.

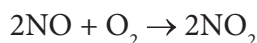
Many boilers are being built with burners designed to reduce nitrogen oxide formation by delaying fuel/air mixing, or distributed fuel addition, thereby establishing fuel-rich combustion zones within the burner whereby the reduced oxygen level maintains a low level of nitrogen oxides production. Other procedures employ ammonia to reduce the nitrogen oxides by injection of ammonia and oxygen into the post combustion zone:



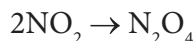
Nitrogen compounds must be absorbed in several chemical and related processes, the most important of which is the absorption of nitrogen peroxide in water for the manufacture of nitric acid. Absorption of nitrous gases also takes place in the lead-chamber process used for the production of sulfuric acid, in the metallurgical industries where metals are treated with nitric acid, and in the purification of several tail gases.

It is also worth, at this point to give some consideration to the production of nitric acid from nitric oxide (using simple chemistry), as might be envisaged in the formation of nitrous and nitric acids in an industrial setting or even in the atmosphere; this latter phenomenon would result in the deposition of acid rain.

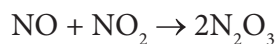
Thus, nitric oxide is oxidized to nitrogen peroxide:



Dimerization of nitrogen peroxide gives nitrogen tetroxide:



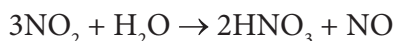
Combination of nitrogen peroxide and nitric oxide gives nitrogen trioxide:



In the presence of water vapor, nitrogen trioxide can be hydrated to nitrous acid:



In the liquid phase, the gross reaction equation of the formation of nitric acid is:



See also: Gas Cleaning, Gas Processing, Gas Treating.

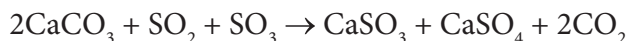
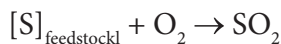
Removal of Sulfur-Containing Gases

Historically, the first method for removing sulfur dioxide from flue gases consisted of water scrubbing the flue gas to absorb sulfur dioxide into solution, and the method was first used in London during the 1930s. Since then, various regulatory organizations in many countries have set standards for sulfur dioxide emissions which must be met.

Sulfur dioxide represents a high percentage of the sulfur oxide pollutants generated in combustion. The removal of the sulfur dioxide from the combustion gases before they are released to the stack is essential, and a considerable number of procedures exist for flue gas desulfurization (FGD). These procedures may be classified as wet or dry depending on whether a water mixture is used to absorb the sulfur dioxide or whether the acceptor is dry.

There are a variety of processes which are designed for sulfur dioxide removal from stack gas, but scrubbing process utilizing limestone (CaCO_3) or lime [$\text{Ca}(\text{OH})_2$] slurries have received more attention than other stack gas scrubbing processes. Attempts have been made to use dry limestone or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) within the combustor

as an in situ method for sulfur dioxide removal, thereby eliminating the wet sludge from wet processes. This involves injection of dry carbonate mineral with the coal followed by recovery of the calcined product along with sulfite and sulfate salts:

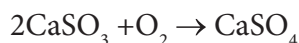
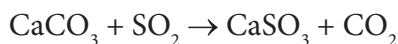


The majority of the stack gas scrubbing processes are designed to remove sulfur dioxide from the gas streams; some processes show the potential for removal of nitrogen oxide(s). However, there is the current line of thinking that pursues the options which enable sulfur oxides and nitrogen oxide(s) to be controlled, at least as far as possible, by modification of the combustion process. Sulfur (as already noted) can be removed by injecting limestone, with the coal into a boiler, while modifications of the combustion chamber, as well as methods of flame temperature regulation and techniques that lower combustion temperatures, such as injection of steam into the combustion region, are claimed to reduce emissions of nitrogen oxide(s).

The procedures can be classified further as regenerative or non-regenerative depending upon whether the chemical used to remove the sulfur dioxide can be regenerated and used again or whether the chemical passes to disposal.

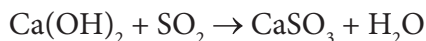
In the wet regenerative processes, either elemental sulfur or sulfuric acid is recovered. In the wet non-regenerative lime and/or limestone procedures, a calcium sulfite or calcium sulfate sludge is produced that is disposed. Wet scrubbing processes contact the flue gas with a solution or slurry for sulfur dioxide removal.

In a wet limestone process, the flue gas contacts a limestone slurry in a scrubber:



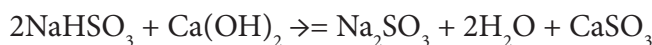
Both the sulfite and the sulfate absorb water of hydration to form the sulfite/sulfate sludge.

In a wet lime process, a gas stream containing the sulfur dioxide is reacted with a wet lime slurry to form the sulfite:



There is subsequent conversion, by oxidation, to the sulfate.

In the double alkali non-regenerative procedure, flue gas is scrubbed with a soluble alkali such as sodium sulfite which is subsequently regenerated with lime to form insoluble calcium sulfite:



Disposal of the calcium sulfite slurry occurs, and the spent absorbent, sodium bisulfite, is regenerated by thermal means:

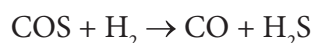


In all of these procedures, water exits the system as vapor in the flue gas.

In either the lime/limestone or sodium sulfite/lime scrubbing processes, the hydrated calcium sulfite and calcium sulfate can be of some environmental concern when the issue of disposal arises. This has, more than anything else, promoted efforts to develop alternate dry scrubbing procedures for the removal of sulfur dioxide. The dry systems have the additional advantage of reducing the pumping requirements necessary for the wet systems.

The tendency to advocate the use of dry lime scrubbing systems thereby produces a waste stream that can be handled by conventional fly ash removal procedures. There are also dry processes, such as the metal oxide processes, in which sulfur dioxide can be removed from gas streams by reaction with a metal oxide. These processes, which are able to operate at high temperatures (approximately 400°C; 750°F), are suitable for hot gas desulfurization without an energy-wasteful cooling step. The metal oxides can usually be regenerated by aerial oxidation, to convert any metal sulfide(s) back to the oxide(s) or by use of a mixture of hydrogen and steam.

The removal of carbonyl sulfide from gas streams, especially those that are destined for the manufacture of synthesis gas, has also been investigated using the principle of hydrogenation:



See also: Gas Cleaning, Gas Processing, Gas Treating.

Renewability

An energy resource is considered renewable if natural processes are constantly replenishing it. Wind, sunshine, geothermal heat, wave power, and wood are typical renewables. However, fossil fuels can also be renewable over many millions of years; some observers believe that geological processes are continually generating new crude oil, though not fast enough to refill oil fields as they are drawn down. Standard renewables, on the other hand, cannot be renewed perpetually because the Sun itself will not last forever. For these and other reasons, some scientists prefer to define renewability in terms of the ongoing human relationship to a given energy resource.

The renewability of a resource in terms of the rate at which humans exploit it compared to the rate at which nature renews it. On this view, there are many resources that are renewable under some conditions of use, but not all. If the resource is regenerated at a higher rate than it is used, it is considered renewable, but if it is exploited at a higher rate than it is regenerated, it is considered non-renewable. The renewability of an energy resource can change, therefore, depending on human activity. For example, wood used as fuel is currently a non-renewable resource wherever humans are logging forests more quickly than new timber is growing. However, if growth were to increase or cutting decrease, fuel wood would eventually become renewable again.

Renewability is a key parameter for evaluating energy technologies according to their environmental impact. The more renewable an energy resource is (that is, the faster it can be regenerated at the level it is being used), the less of an environmental impact it has. At present, coal is a non-renewable resource as it takes many millions of years for it to form. It is unlikely that the renewability of this resource is going to change due to coal's high level of exploitation by humans and its extremely slow rate of regeneration.

Wind electricity, however, has high renewability, as there is essentially no time lag between its use and regeneration. On these grounds alone, one would expect coal mining to have a greater environmental impact than wind generation. Exploitation of forests at rates low enough to permit renewal would likewise be expected to have less environmental impact than exploitation above renewal rates.

Coal and wind are extremes of low renewability and high renewability. It is of most interest to examine what energy technologies have intermediate renewability that can be realistically increased by policy choices. Renewability might be increased by more efficient use of a resource (e.g., wood), allowing lower harvesting rates. It might also, in a technical sense, be increased by discovering how to turn a non-resource renewable material into a useful resource.

See also: Renewable Energy.

Renewable Energy

Renewable energy is any form of energy obtained from natural resources, such as biomass, geothermal heat, ocean energy, and wind. However, there are many different types of energy. Kinetic energy is energy available in the motion of particles, and wind energy is one example of this. Potential energy is the energy available because of the position between particles, such as water stored in a dam, the energy in a coiled spring, and energy stored in molecules (gasoline). There are many examples of energy: mechanical, electrical, thermal, chemical, magnetic, nuclear, biological, tidal, and geothermal. Renewable energy denotes a clean, nontoxic energy source that cannot be exhausted. In fact, renewable energy is no longer a niche sector, promoted only by governments and environmentalists. Public concern about climate change and protection of the environment, coupled with depletion of fossil energy reserves and environmental issues are driving increasing rates of investment into research for clean and cost-effective forms of energy.

The primary renewable energy sources are the Sun, wind, biomass, tides, waves, and the heat of the Earth (geothermal). Solar energy is referred to as renewable and/or sustainable energy because it will be available as long as the Sun continues to shine. Estimates for the life of the main stage of the Sun are another 4 to 5 billion years. Wind energy is derived from the uneven heating of the surface of the Earth due to more heat input at the equator with the accompanying transfer of water by evaporation and rain. In this sense, rivers and dams for hydro-energy are stored solar energy. Another aspect of solar energy is the conversion of sunlight into biomass by photosynthesis. Animal products such as whale oil and biogas from manure are derived from this form of solar energy.

Tidal energy is primarily due to the gravitational interaction of the Earth and the moon. Another renewable energy is geothermal, due to heat from the Earth generated by decay of radioactive particles from when the solar system formed. Volcanoes are fiery examples of geothermal energy reaching the surface of the Earth from the hot and molten interior. Overall, a growing source of energy is biomass – primarily wood and charcoal, but also crop residue and even animal dung for cooking and some heating. This contributes to deforestation and the loss of topsoil in developing countries.

Fossil fuels are stored solar energy from past geological ages (i.e., ancient sunlight). Even though the quantities of oil, natural gas, and coal are large, they are finite and resources are sufficient to power the industrialized world anywhere from a few more decades to a few more centuries, depending on the resource. There are also large environmental costs associated with fossil fuel exploitation, from habitat loss and destruction due to strip mining and oil spills to global warming of the atmosphere largely caused by the combustion by-product of carbon dioxide.

The advantages of renewable energy are many: sustainability (cannot be depleted), ubiquity (found everywhere across the world in contrast to fossil fuels and minerals), and essentially nonpolluting and carbon-free. The disadvantages of renewable energy are variability, low density, and generally higher initial cost for conversion hardware. For different forms of renewable energy, other disadvantages or perceived problems are visual pollution, odor from biomass, perceived avian issues with wind plants, large land requirements for solar conversion, and brine from many geothermal sources.

Renewable Energy – Sources

Renewable energy, often referred to as clean energy, comes from natural sources or processes that are constantly replenished. Renewable energy sources include (alphabetically rather than by common use or preference) (i) biomass, (ii) geothermal energy, (iii) hydroelectric energy, (iv) ocean energy, (v) solar energy, and (vi) wind energy.

Renewable energy provides substantial benefits for the climate but, like fossil fuel energy, are not without some effects on the environment, some of which may be considered to be significant. The exact type and intensity of environmental impacts varies depending on the specific technology used, the geographic location, and a number of other factors. By understanding the current and potential environmental issues associated with each renewable energy source, steps can be taken to avoid or at least minimize these impacts as they become a larger portion of the supply of electrical energy.

Despite the environmental impacts, renewable energy technologies compare extremely favorably to fossil fuels, and remain a core part of the solution of climate change issues.

Biomass

Biomass is organic material that comes from plants and animals, and includes crops, waste wood, and trees. Sources of biomass for producing electricity are diverse, ranging from energy crops (like switchgrass), to agricultural waste, manure, forest products and waste, and urban waste. Both the type of feedstock and the manner in which it is developed and harvested significantly affect land use and life-cycle global warming emissions impacts of producing power from biomass.

When biomass is burned, the chemical energy is released as heat and can generate electricity with a steam turbine. Biomass power plants share some similarities with fossil fuel power plants: both involve the combustion of a feedstock to generate electricity. Thus, biomass plants raise similar, but not identical, concerns about air emissions and water use as fossil fuel plants. However, the feedstock of biomass plants can be sustainably produced, while fossil fuels are non-renewable.

Biomass is often mistakenly described as a clean, renewable fuel and a greener alternative to coal and other fossil fuels for producing electricity. However, many forms of biomass – especially from forests – produce higher carbon emissions than fossil fuels. There are also negative consequences for biodiversity. However, some forms of biomass energy could serve as a low-carbon option under the right circumstances. For example, sawdust and chips from sawmills that would otherwise quickly decompose and release carbon can be a low-carbon energy source.

Geothermal

Geothermal technology is a new take on a recognizable process—the coils at the back of your fridge are a mini heat pump, removing heat from the interior to keep foods fresh and cool. In a home, geothermal or geo-exchange pumps use the constant temperature of the earth (a few feet below the surface) to cool homes in summer and warm houses in winter and also to heat water.

The core of the Earth is a source of heat due to the slow decay of radioactive particles in rocks at the center of the planet. Drilling deep wells brings hot underground water to the surface as a hydrothermal resource, which is then pumped through a turbine to create electricity.

Hydroelectric Power

Hydropower relies on water – typically fast-moving water in a large river or rapidly descending water from a high point – and converts the force of the water into electricity by spinning the turbine blades of a generator.

However, large hydroelectric plants – and the accompanying mega-dams – divert and reduce natural water flows, thereby restricting access for animal and human populations that rely on rivers.

Ocean Energy

Tidal and wave energy is still in a developmental phase, but the ocean will always be ruled by the moon's gravity, which makes harnessing its power an attractive option. Some tidal energy approaches may harm wildlife, such as tidal barrages, which work much like dams and are located in an ocean bay or lagoon. Like tidal power, wave power relies on dam-like structures or ocean floor-anchored devices on or just below the surface of the water.

Solar Energy

Solar cells (or photovoltaic cells) are made from silicon or other materials that transform sunlight directly into electricity. Distributed solar systems generate electricity locally for homes and businesses, either through rooftop panels or community projects that power entire neighborhoods. Solar farms can generate power for thousands of homes, using mirrors to concentrate sunlight across acres of solar cells. Floating solar farms (sometimes referred to as floatovoltaics) can be an effective use of wastewater facilities and bodies of water that are not ecologically sensitive.

Solar energy systems don't produce air pollutants or greenhouse gases, and as long as they are responsibly sited, most solar panels have few environmental impacts beyond the manufacturing process.

Wind Energy

Wind energy (or wind power) describes the process by which wind is used to generate electricity. Wind turbines convert the kinetic energy in the wind into mechanical power.

In the process, the wind energy turns turbine blades, which feeds an electric generator and produces electricity through turbines which can be placed anywhere with high wind speeds, such as hilltops and open plains or even offshore in open water.

Renewable Natural Gas

Renewable natural gas is a biogas which has been upgraded to a quality similar to natural gas. A biogas is a gas obtained from biomass. By upgrading the quality to that of natural gas, it becomes possible to distribute the gas to customers via the existing gas grid, and burned within existing appliances. Renewable natural gas is also known as sustainable natural gas, and is a subset of synthetic natural gas or substitute natural gas (SNG).

Renewable natural gas can be produced economically, and distributed via the existing gas grid, making it an attractive means of supplying existing premises with renewable heat and renewable gas energy, while requiring no extra capital outlay of the customer. The existing gas network allows distribution of gas energy over vast distances at a minimal cost in energy. Existing networks would allow biogas to be sourced from remote markets that are rich in low-cost biomass (Russia or Scandinavia for example).

In terms of the present context, renewable natural gas can be manufactured through two main processes which are (i) anaerobic digestion of organic (normally moist) material or (ii) thermal gasification of organic (normally dry) material that has been mined from the landfill. In both cases, the gas from primary production has to be upgraded in a secondary step to produce gas that is suitable for injection into the gas grid.

See also: Biogas, Natural Gas.

Research Octane Method

The research octane method (ROM) is a test method for determining the knock rating, in terms octane numbers, of fuels for use in spark-ignition engines. The data from test method are used in conjunction with the data from the Motor Octane Test Method to determine the octane number.

The research octane method (ASTM D908) measures the octane number of a gasoline under relatively mild, low-speed operating conditions. The motor octane method (ASTM D357) measures the octane number of a gasoline under the load of high revolutions per minute and elevated temperature.

See also: Octane Number., Octane Rating.

Reserves

At some time during the exploration or development processes, certain resources may become reserves. Such a reclassification can arise as a result of improvements in recovery techniques which may either make the resource accessible or cause a lowering of the recovery costs and render winning of the resource an economical proposition. In addition, other uses may also be found for a commodity, and the increased demand may result in an increase in price. Alternatively, a large deposit may become exhausted and unable to produce any more of the resource, thus forcing production to focus on a lower-grade, high-recovery-cost resource. More specifically, the use of the term reserves as being descriptive of the resource is subject to much speculation and, in fact, is subject to word variations. For example, reserves are classed as proved, probable, possible, and potential (Table R-15).

Table R-15 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Proved reserves are those reserves of the mineral that have been positively identified as recoverable with current technology. Probable reserves are those reserves of the mineral that are nearly certain but a slight doubt does exist. Possible reserves are those reserves where there is an even greater degree of uncertainty but there is some information.

Potential reserves are based upon geological information related to the types of sediments where such resources are likely to occur, and they are considered to represent an educated guess. Also, there are the so-called undiscovered reserves which are lacking specific data and are often subject to speculation – some observers would say that these types of reserves are a little more than figments of imagination! Thus, in reality, and in spite of the use of self-righteous wordsmithing, the proved reserves may be a small part of the total hypothetical and/or speculative amounts of a resource.

See also: Resources and Reserves

Residual Herbaceous Biomass

Residual herbaceous biomass (straw) is the main residual herbaceous material for energy application. As it is a residual product, its availability for energy purposes is driven by the cereals markets and does not have autonomous market behavior. In addition, farms consume significant quantities of straw internally – as bed material for livestock, grain drying, etc. Some straw is also chaffed and returned back to the field as soil ameliorator. The net straw yield per hectare for energy application also depends on the crop, the grain yield per hectare, climate and cultivation conditions, etc. Nevertheless, one can roughly estimate that the average straw yield per hectare is approximately 50 to 65% of the grain yield per hectare from cereals and oilseeds.

Similar to herbaceous crops, straw usually has lower moisture content than woody biomass. Conversely, it has a lower calorific value, bulk density, ash melting point and higher content of ash, and problematic inorganic component such as chlorine, potassium, and sulfur, which cause corrosion and pollution. The last two drawbacks can be relatively easily overcome by leaving straw on the field for a while. In such a way, rainfall provides a natural leaching process and separates a large part of the potassium and the chlorine. Alternatively, fresh straw can be directly shipped to the gasification plant, where it is washed by dedicated facilities at moderate temperatures (50 to 60°C; 120 to 140°F). Due to washing, the initially low moisture content of straw becomes higher in both cases, and hence a mandatory drying is applied afterwards. In both cases also, the content of corrosive components is reduced, but not completely taken out. In order to decrease handling costs, straw and dedicated herbaceous energy crops are usually baled before being shipped to the gasification plant. The weight and the size of bales depend on the baling equipment and on the requirements of the gasification plant.

There are many opportunities for producing fuel from agricultural crops and crop residues. Possible end products include ethanol, vegetable oil, and solid cellulosic fuels. Ethanol can be produced from any grain, root, fruit, or juice crop containing fermentable carbohydrates. It also can be made from crops, residues, or wood that contain cellulose or other long-chain carbohydrates which can be hydrolyzed to fermentable sugars.

Vegetable oils are produced from numerous oil seed crops. Some of these oils have been evaluated in other laboratories as substitutes for diesel fuel. While all vegetable oils have high energy content, most require some processing to assure safe use in internal combustion engines.

The simplest form of agricultural biomass energy use involves direct combustion of cellulosic crops or residues, such as hay, straw, or corn fodder, to heat space or produce steam. Such fuels are useful for heating farm buildings and small commercial buildings in rural areas and for drying crops. Ideally, energy crops should be produced on land not needed for food production. This use should not increase the erosion hazard or cause other environmental damage. On the other hand, a variety of crops can be grown specifically to provide sources of energy, and once established, a stand of perennial biomass/energy crop is expected to remain productive for a period of 6 years or more.

See also: Agricultural Residues, Agricultural Waste, Biomass.

Residual Woody Biomass

Residual wood is the material that is a refuse without objective value within a specific context; otherwise, it constitutes a material at the end of its usefulness. Thus, a number of woody materials can be included in the group of residues and waste: thinning and logging residues from forest industry (tops, branches and small size stems), demolition wood and railway sleepers, fiberboard residues, cutter shavings, and plywood residues. Residual woody material is believed to be a very promising bioenergy resource since it is available at much lower or negligible cost compared to wood logs and short-rotation forestry.

The availability of residual woody biomass depends on the primary wood yield and typically accounts for 25 to 45% of all harvested wood on average. The heterogeneous composition of the residual and waste woody biomass (content of moisture and impurities) may preclude using this type of biomass for biomass-to-liquids production. Preliminary treatment of the residual and waste woody biomass may be necessary, in order to make it appropriate for processing to liquid fuels.

A residual (waste) product can be defined as a material, which is a refuse without objective value within a specific context; otherwise, it constitutes a material at the end of its usefulness. Ensuing from this definition, a number of woody materials can be included in the group of residues and waste: thinning and logging residues from forest industry (tops, branches, and small-size stems), demolition wood and railway sleepers, fiberboard residues, cutter shavings, and plywood residues. Residual woody material is believed to be a very promising bioenergy resource since it is available at much lower or negligible cost compared to wood logs and short-rotation forestry.

See also: Agricultural Residues, Agricultural Waste, Biomass, Residual Herbaceous Biomass, Wood, Wood Biomass.

Residues

See also: Agricultural Residues, Agricultural Waste, Residual Woody Biomass.

Resources and Reserves

Resources are those usable materials that occur naturally within the Earth and are often referred to as natural resources which are usually either (i) non-renewable or (ii) renewable (Table R-16).

The former category refers to those resources which are, as the name implies, those resources that are no longer available once the available resource at a site is exhausted. In general terms, the development of resources is usually concerned with the production or use of energy.

Table R-16 An example of the general categorization of natural resources.

Resource category	Type	Name
Non-renewable	Fossil	Natural gas
		Crude oil
		Heavy crude oil
		Extra heavy crude oil
		Tar sand bitumen
	Minerals (nuclear examples)	Coal
		Oil Shale
		Uranium
		Thorium
		Clay minerals
Fluorine minerals		
Silica		
Sulfur minerals		
Renewable*	Biomass	Wood
		Grasses
		Crops
		Algae
		Aquatic plants
	Geothermal	Natural steam
		Hot water
		Volcanic heat
	Oceans	Ocean heat
		Ocean current
		Wave energy
	Solar	Solar-thermal conversion
		Photochemical energy
		Photoelectric energy
		Stored solar heat
	Tidal	Tidal energy
	Wind	Electric energy

*Listed alphabetically and not in any order of popularity of preference.

These resources have been useful to humans in a variety of ways, either directly in the original form (such as coal) or indirectly after certain modification (such as crude oil products). At one time, the Earth was believed to have an inexhaustible supply of natural resources. But it is no longer realized that some resources (the fossil fuels, environmental issues notwithstanding) are unlimited or inexhaustible – some resources are renewable while others are not.

Humans have been exploiting major groups of resources (including non-fossil fuels resources) which have now been depleted to an irreparable extent (Jazib, 2018). Mineral resources, which are non-renewable and include the fossil fuels (natural gas, crude oil, and coal). The fossil fuel sources are carbonaceous resources which are formed from the fossilized remains of prehistoric organisms, and are also considered non-renewable. Fossil fuels currently account for the majority of the total energy consumption of the world, and this is projected to continue for the next several decades. On the other hand, natural renewable resources, such as wind and water, have been used throughout history, and until recently were a predominant energy source.

It is pertinent to consider the use of natural resources since the onset of the Industrial Revolution in the late 1700s, when the use of the natural resources of the Earth which has focused on the production of energy. Therefore, it is necessary to understand the relationships that exist between a natural resource, the commodity produced from that resource, and the environment which can be represented by a simple equation of progression from one to the other:

$$\text{Natural resource} \rightarrow \text{commodity} \rightarrow \text{environment}$$

Perturbations in one aspect of this equation typically usually cause perturbations in one, or both, of the other two. For example, the availability of many metals depends upon the quantity of energy used and the amount of environmental damage tolerated in the extraction of low-grade ores. Mining and processing of resources offer the world valuable commodities suitable for a variety of industrial and domestic uses as well as a variety of contaminants. In addition, production and use may also involve major environmental concerns, including disturbance of land, air pollution from dust and smelter emissions, and water pollution from disrupted aquifers. This problem is aggravated by the fact that the general trend in mining involves utilization of less rich ores, almost analogous to the acceptance by refineries of lower-quality crude oil such as heavy crude oil as well as extra heavy crude oil and tar sand bitumen (Table R-17).

Table R-17 Simplified descriptions of conventional crude oil, tight oil, heavy crude oil, extra heavy crude oil, and tar sand bitumen*.

Conventional Crude Oil Mobile in the reservoir; API gravity: >25° High-permeability reservoir Primary recovery Secondary recovery
Tight Oil Similar properties to the properties of conventional crude oil; API gravity: >25° Immobile in the reservoir Low-permeability reservoir Horizontal drilling into reservoir Fracturing (typically multi-fracturing) to release fluids/gases
Heavy Crude Oil More viscous than conventional crude oil; API gravity: 10-20° Mobile in the reservoir High-permeability reservoir Secondary recovery Tertiary recovery (enhanced oil recovery – EOR, e.g., steam stimulation)

(Continued)

Table R-17 Simplified descriptions of conventional crude oil, tight oil, heavy crude oil, extra heavy crude oil, and tar sand bitumen*. (Continued)

Extra Heavy Crude Oil Similar properties to the properties of tar sand bitumen; API gravity: <10° Mobile in the reservoir High-permeability reservoir Secondary recovery Tertiary recovery (enhanced oil recovery – EOR, e.g., steam stimulation)
Tar Sand Bitumen Immobile in the deposit; API gravity: <10° High-permeability reservoir Mining (often preceded by explosive fracturing) Steam-assisted gravity draining (SAGD) Solvent methods (VAPEX) Extreme heating methods Innovative methods**

*This list is not intended for use as a means of classification.

**Innovative methods exclude tertiary recovery methods and methods such as steam-assisted gravity drainage (SAGD) and vapor-assisted extraction (VAPEX) methods but do include variants or hybrids thereof.

However, before launching into a description of the various natural resources, it is necessary to understand how the reserves of these natural resources are defined. A resource is the entire commodity that exists in the sediments and strata, whereas the reserves represent that fraction of a commodity that can be recovered economically. On the other hand, reserves are that subgroup of a resource that has been discovered, has a known size, and can be extracted economically. Factors that affect whether or not reserves can be extracted economically include (i) the demand, (ii) market price, (iii) mining costs, transportation costs, (iv) new technologies that can extract the material at a lower price, (v) taxes, (vi) environmental laws, and (vii) government price controls. Understandably, the economic value of a resource can change with time as these factors change.

Thus, at some time in the future, certain resources may become reserves. Such a reclassification can arise as a result of improvements in recovery techniques which may either make the resource accessible or cause a lowering of the recovery costs and render winning of the resource an economical proposition. In addition, other uses may also be found for a commodity, and the increased demand may result in an increase in price. Alternatively, a large deposit may become exhausted and unable to produce any more of the resource, thus forcing production to focus on a lower-grade, high-recovery-cost resource. More specifically, the use of the term reserves as being descriptive of the resource is subject to much speculation and, in fact, is subject to word variations. For example, reserves are classed as proved, probable, possible, and potential (Table R-18).

Table R-18 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

Proved reserves are those reserves of the mineral that have been positively identified as recoverable with current technology. Probable reserves are those reserves of the mineral that are nearly certain but a slight doubt does exist. Possible reserves are those reserves where there is an even greater degree of uncertainty but there is some

information. Potential reserves are based upon geological information related to the types of sediments where such resources are likely to occur and they are considered to represent an educated guess. Also, there are the so-called undiscovered reserves which are lacking specific data and are often subject to speculation – some observers would say that these types of reserves are a little more than figments of imagination! Thus, in reality, and in spite of the use of self-righteous wordsmithing, the proved reserves may be a small part of the total hypothetical and/or speculative amounts of a resource.

Reverse Osmosis

The reverse osmosis process is, as the name implies, based on reversing the solvent flow that would normally be caused by osmosis through a semipermeable membrane, i.e., one which would pass solvent but retain solute. This is achieved by applying a sufficiently large pressure drop across the membrane so that flow occurs in a direction opposite to that expected for osmosis.

Using a brine solution, if a semipermeable membrane that will pass water but not salt is placed on one side of the membrane and pure water on the other side of the membrane, the pure water will flow through the membrane which will raise the liquid level in the left arm and thus the pressure on the left side of the membrane until an equilibrium is established. Equilibrium occurs when the additional pressure caused by the rising liquid level on the relevant side of the membrane is adequate to prevent any further flow of pure water through the membrane. The additional pressure (the osmotic pressure of the salt solution) is a consequence of the difference in chemical potential between the brine solution and pure water. On the other hand, a sufficiently long column of brine is used at the beginning of the process, and this column of water offsets the osmotic pressure of the brine solution; no flow of pure water in either direction will occur. The pressure differential across the barrier under these conditions is the osmotic pressure of the brine.

Thus, in order for the reverse to occur, the pressure gradient opposing the osmotic pressure must be greater than the osmotic pressure so that the flow of pure water will actually be from left to right through the membrane. The required pressure drop across the membrane is the sum of the pressure needed to overcome osmotic pressure to prevent reverse flow and the pressure drop required to get reasonable flow rates. This depends on the concentration of impurities in the water phase.

See also: Gas Cleaning, Gas Processing, Gas Treating, Membrane Systems, Membrane Technology, Microfiltration, Ultrafiltration.

Reversible Chemical Reactions

Reversible chemical reactions can be extremely selective for the separation of materials on the basis of their chemical reactivity. An example is the removal of acid gases such as carbon dioxide or sulfur dioxide from a variety of gas streams. When the gas stream is scrubbed with an aqueous alkaline solution, the acid gases react with the solution to form soluble salts which stay dissolved in the liquid phase. The non-reactive components of the flue gas are not dissolved and continue on the chosen path. The separation factor between reactive and non-reactive components in the feed is theoretically infinite and in practice achieves values approaching 100. That is, one theoretical stage of separation will separate a 50:50 feed mixture into a 99% pure product mixture. There are many types of reversible chemical separations, one of the oldest being the separation of various organic molecules by extraction with sulfuric acid of different strengths.

The material used as the reactive separating agent can be used either as a solid or a liquid. If it is applied as a solid to form a solid product, the process is very similar to adsorption and ion exchange. In this case, the reagent is usually supported on a solid carrier to get high surface area. It is also frequently incorporated into a polymer resin in much the same way as the active sites in an ion exchange resin. However, it can also be used as a simple solid reagent where it is insoluble in the feed stream and forms a reaction product which is also insoluble in the treated product stream. When the chemical reagent is applied as a liquid or solution to form a product soluble in the reagent, the separation process is very similar to solvent extraction when treating a liquid, and absorption or scrubbing when treating a gas.

See also: Adsorption, Ion-exchange.

Rhizosphere

The rhizosphere is a dynamic region governed by complex interactions between plants and the organisms that are in close association with the root. The composition and pattern of root exudates affect microbial activity and population numbers, which in turn have an impact on the nematodes and microarthropods that share this environment. Beneficial or harmful relationships exist between rhizosphere organisms and plants, which ultimately affect root function and plant growth. In addition, the rhizosphere may include organisms that do not directly benefit or harm plants but clearly influence plant growth and productivity.

A better understanding of the soil–root and soil–seed interface is needed to manage microorganisms, increase plant growth, and reduce the impact of plant production, agriculture, and fuel discharge on the environment. The benefits of studying the rhizosphere include the use of plant growth-promoting organisms and the suppression of plant diseases and weeds using biocontrol agents. Rhizosphere organisms can also be used to enhance the formation of stable soil aggregates and as bioremediation agents of contaminated soils. With greater understanding of the ecology and biota in the rhizosphere, this zone of increased nutrients, biotic activity, and interactions can be manipulated to improve plant productivity and environmental quality.

See also: Soil.

Rice Straw

Agricultural crop residues such as straw are a valuable renewable biomass resource. Silica, alkali minerals, and other undesirable characteristics of these crop residues make certain parts of the straw more or less valuable as bioenergy feedstocks. The use of rice straw for producing materials, fuels, and chemicals has been limited in part by the cost of pretreating straw biomass to make it a suitable feedstock for bioenergy conversion.

Rice straw is one of the so-called cereal straws and contains a low concentration of lignin. Rice straw has a higher silica content (as high as 18% w/w in clean rice straw and 19 to 24% w/w including silica from field dust) than other cereal straws, which makes pulping somewhat more costly due to increased chemical recovery difficulties and costs.

Recent developments in pre-pulp cleaning and pulping techniques have yielded much higher precipitation of silica from the pulping waste (also called black liquor), making chemical recovery more viable, and thereby diminishing pulping costs. Researchers have also identified new uses for the recovered silica, which can be made into bricks, ceramic articles, and glassware, thus completing the recovery cycle.

The quantity of straw available for removal from a field is dependent upon the amount that must be left to insure long-term sustainable crop production.

Straw can be converted to ethanol fuel. Determining the volume of fuel that could be produced depends on both the quantities of available straw and the technology used to convert the straw to ethanol. The amount of straw available depends on how much is produced each year and how much can be recovered while maintaining soil fertility.

See also: Agricultural Residues, Agricultural Waste, Straw, Wheat Straw.

Rotary Kiln Incinerator

The rotary kiln incinerator has a primary chamber and a secondary chamber. The primary chamber consists of an inclined refractory-lined cylindrical tube. Movement of the cylinder on its axis facilitates movement of waste. In the primary chamber, there is conversion of solid fraction to gases, through volatilization, destructive distillation, and partial combustion reactions. The secondary chamber is necessary to complete gas-phase combustion reactions.

The clinker spills out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases may be combusted in an afterburner. To control air pollution, the combustion product gases are further treated with acid gas scrubbers to remove sulfuric acid and nitric acid emissions, and then routed through bag houses to remove particulates before the gases are released into the atmosphere.

See also: Combustion, Incinerators.

Rotation

Rotation (sequencing) is the period of years between the establishment of a stand of timber and the time when it is considered ready for final harvest and regeneration.

Crop rotation (crop sequencing) is the practice of growing a series of dissimilar types of crops in the same area in sequential seasons for various benefits such as to avoid the buildup of pathogens and pests that often occurs when one species is continuously cropped. Crop rotation also seeks to balance the fertility demands of various crops to avoid excessive depletion of soil nutrients.

It also means that the succeeding crop belongs to a different family than the previous one. The planned rotation may vary from 2 or 3 years or a longer period.

As in the production of crops for agricultural use, the production of crops as sources of biofuels, rotation will also be necessary to ensure the replenishment of the soil and the growth of useful biomass.

Crops are selected that produce sufficient quantities of biomass at the appropriate time to reduce erosion by water or wind to within acceptable soil loss levels. The amount of biomass needed shall be determined using prediction technology.

See also: Crops, Energy From Crops.

Round Wood Products

Round wood products are logs and other round timber generated from harvesting trees for industrial or consumer use.

While there are primary use (usually poles, posts, piles) for round wood products, forest-based woody biomass includes round wood products and logging residue and can also be used as biomass for a biomass-to-energy plant.

See also: Residual Woody Biomass, Wood Biomass.

RTP Process

The RTP process (rapid thermal processing) involves rapid heating of biomass in the absence of oxygen. The biomass is vaporized and then rapidly cooled to generate high yields of pyrolysis oil (Table R-19). The process utilizes a circulating transported fluidized bed reactor system similar to that used in the fluid catalytic cracking technology. The pyrolysis oil can then be burned for energy in industrial burners and furnaces for heat or used to generate electricity.

Table R-19 Yields and quality of pyrolysis oil from various feedstocks.

Biomass	Yield, % w/w	Heating value, Btu/lb
Hardwood	70-75	7,400–8,200
Softwood	70-80	7,300–8,000
Hardwood Bark	60-65	7,180–8,680
Softwood Bark	55-65	7,180–8,500
Corn Fiber	65-75	7,570–8,680
Bagasse	70-75	8,100–8,200
Waste Paper	60-80	7,300–7,400

The pyrolysis oil has virtually no sulfur and can be adapted for use in a wide variety of industries including electrical generation, forestry, refining and petrochemicals, pulp and paper, and the most energy-intensive heavy industry.

In addition to pyrolysis oil, the process also produces char and a non-condensable gas, both of which can be used to provide process energy in the reheater to maintain the process and/or in the dryer to condition the biomass.

See also: Fluid Catalytic Cracking, Pyrolysis, Thermal Decomposition.

Saponification Value

The saponification value (SV, or saponification number, SN) represents the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of fat under the conditions specified in the test method. The value is a measure of the average molecular weight (or chain length) of all of the fatty acids present in the sample as triglycerides. The higher the saponification value, the lower the fatty acids average length, the lower the mean molecular weight of triglycerides and the converse is also true – i.e., the lower the saponification value, the higher the average length of the fatty acids present in the sample as triglycerides.

To determine saponification value, the sample is hot-saponified with an excess of alkali (usually potassium hydroxide dissolved in ethanol), in standard conditions, generally for half an hour under reflux. Alkali is mainly consumed by glycerides (monoglycerides, diglycerides) and triglycerides as well as by free fatty acids and other ester-type components such as lactones. At the end of the reaction, the remaining quantity of alkali is titrated against the standard solution of hydrochloric acid (HCl). The saponification value (SV, mg KOH/ g of sample) is calculated by the following equation:

$$SV = [(B-S) \times M \times 56.1]/W$$

In the equation, (B-S) is the difference between the volume of HCl solution used for the blank run and for the tested sample, in mL, M is the molarity of HCl solution, in mol L⁻¹, 56.1 is the molecular weight of KOH, in g mol⁻¹, and W is the weight of sample, in g.

See also: Acid Number, Fatty Acid, Neutralization Number.

Sasol Slurry Phase Reactor

The Sasol slurry phase reactor uses a slurry bubble column (and sometimes referred to as a bubble phase reactor) was a development to convert coal to liquid products using the Fischer-Tropsch process. The reactor is essentially a vessel containing a slurry comprising catalyst dispersed in the wax produced by the Fischer-Tropsch synthesis.

In the process, synthesis gas is bubbled through this slurry and is converted to hydrocarbons. The heat generated is transferred from the slurry to the cooling coils inside the reactor to generate steam. The low-boiling hydrocarbon derivatives in the vapor phase are removed from the freeboard at the top of the SPR together with the unconverted reactants before being condensed in the downstream cooling train. The higher-boiling liquid hydrocarbon derivatives are part of the slurry from which they must be removed by means of a solid separation process. The successful development of an effective and relatively cheap liquid–solid separation step is crucial to the development of the slurry phase reactor, and the catalyst is sufficiently strong to prevent excessive attrition.

A characteristic of the slurry phase reactor is that the liquid phase is well mixed and can operate virtually isothermally. The absence of axial and radial temperature gradients, as is the case in a fixed-bed reactor, allows for much higher average operating temperatures in the slurry phase reactor and therefore higher reaction rates. In addition, a highly active catalyst can be accommodated, since the limitations of intra-particle diffusion are avoided by applying relatively small size (20–300 µm) of the catalyst particles sizes without adverse pressure drop consequences.

The slurry phase reactor allows for on-line catalyst withdrawal and addition, which is not feasible with a fixed bed reactor. This is especially important for iron-catalyzed Fischer-Tropsch synthesis where the catalyst must be replaced periodically. In the case of non-iron catalysts, this is of lesser importance, but the addition and withdrawal features can also be used in combination with regeneration or rejuvenation of a cobalt-based catalyst outside the reactor when reactivation of the catalyst inventory is required.

See also: Slurry Phase Reactor, Synthesis Gas.

Sawdust Briquettes

Briquettes produced from biomass residues and from agricultural residues are a good substitute for firewood. Also, the formation of briquettes at the very site of its production stops air pollution to a large extent. Hence briquetting of sawdust produces a renewable and environmentally friendly source of energy.

Sawdust is waste material from all types of primary and secondary wood processing. Between 10 and 13% of a log is reduced to sawdust in milling operations. Sawdust is bulky, and is therefore expensive to store and transport. Also, the calorific value of sawdust is quite low, so that briquetting is an ideal way to reduce the bulk, to increase the density, and thus to increase the calorific value. The equipment required for producing sawdust briquettes consist of a drier, a press, and an extruder with a tapered screw and a large revolving disk.

Sawdust briquettes are formed under sufficiently high pressure to produce cohesion between wood particles. In the process, the lignin softens and binds the briquette, so no additional binder is required. The use of sawdust briquettes has several advantages, including (i) the price which is usually approximately the same as fuel wood but is much more convenient to use as they do not require further cutting and chopping, (ii) the good burning characteristics in any kind of solid fuel stove and boiler, (iii) the quick ignition followed by clean burning and only leaving 1 to 6% w/w ash, (iv) the sulfur-free feedstock which burns without producing an odor, and (v) a high heat content.

See also: Bagasse Briquettes, Briquetting.

SCOT Process

The SCOT process (Shell Claus off-gas treating process) is a tail gas treating process that was developed in the early 1970s and consists of a combination of a catalytic hydrogenation/hydrolysis step and an amine scrubbing unit. The hydrogenation/hydrolysis of the sulfur compounds in the tail gases from the Claus unit has already been covered above.

The early SCOT units consisted of a hydrogenation/hydrolysis reactor and a conventional amine unit. The Claus tail gas, after being reduced in the reactor, is cooled in a quench column and scrubbed by a Sulfinol solution. The clean tail gas goes to a Claus incinerator and the acid gas-rich solution is regenerated in a stripping column. The acid gas off the top of the stripper is recycled back to the Claus plant for further conversion of the hydrogen sulfide. The absorber is operated at near atmospheric pressure, and the amine solvent is not highly loaded with acid gases. Because the solution is not highly loaded, unlike high pressure operation, there is no need for an intermediate flash vessel and the loaded solution goes directly to a stripper.

Early SCOT units used diisopropanolamine in the Sulfinol (Sulfinol-D) solution. Methyl diethanolamine-based Sulfinol (Sulfinol-M) was used later to enhance hydrogen sulfide removal and to allow for selective rejection of carbon dioxide in the absorber.

To achieve the lowest possible hydrogen sulfide content in the treated gas, the Super-SCOT configuration was introduced. In this version, the loaded Sulfinol-M solution is regenerated in two stages. The partially stripped solvent goes to the middle of the absorber, while the fully stripped solvent goes to the top of the absorber. The solvent going to the top of the absorber is cooled below that used in the conventional SCOT process.

The SCOT process can be configured in various ways. For example, it can be integrated with the upstream acid gas removal unit if the same solvent is used in both units. Another configuration has been used to cascade the upstream gas clean-up with the SCOT unit. A hydrogen sulfide-lean acid gas from the upstream gas treating unit is sent to a SCOT process with two absorbers. In the first absorber, the hydrogen sulfide-lean acid gas is enriched, while the second absorber treats the Claus tail gas. A common stripper is used for both SCOT absorbers, and, in this latter configuration, different solvents could be used in both the upstream and the SCOT units.

The SCOT process is adversely affected by high concentrations of carbon dioxide, and since gaseous emissions from oil shale processing are expected to be rich in carbon dioxide, higher rates of recycling, more complete fuel combustion, and perhaps steam injection to dissolve the carbon dioxide may be necessary.

See also Claus Process, Gas Cleaning, Gas Processing, Gas Treating, Sulfinol Process, Tail Gas Cleaning.

Scrap Tires

Tire recycling has become a necessity because of the huge piles of tires that represent a threat to the environment. The used tires represent a source of energy and valuable chemical products. By thermal decomposition of rubber under reduced pressure, it is possible to recover the useful compounds.

To alleviate the problems caused by scrap tire stockpiles, it is essential to adopt appropriate waste management strategy to cope with the increasing amount of scrap tires generated every year. Major ways of utilizing scrap tires, including retreading, recycling (in civil engineering and ground rubber applications), and energy recovery (e.g., through combustion in cement kilns and pyrolysis). The most important methods for sustainable environmental stewardship is converting the tires to bio-oil.

Thermochemical conversion processes are an approach to producing liquids and chemicals from scrap tires. These processes include incineration, hydrothermal liquefaction (HTL), gasification, and pyrolysis that can also be completed in the presence or absence of catalysts.

In the case of gasification – a thermochemical process that converts organic material to a gas mixture (synthesis gas) as well as minor products such as water and char at elevated temperature (800 to 1,000°C, 1,470 to 1,830°F) and partial pressure. Gasification at high temperature and a controlled environment results in converting a great proportion of the biomass into gas products. Gas products mainly include methane, ethane, hydrogen, carbon monoxide, carbon dioxide, and char in addition to a small amount of tar. The synthesis gas is predominantly used in gas turbines and engines to produce electricity.

Gasification reactors come in various styles such as fixed bed, fluidized bed, and entrained bed reactors.

See also: Gasifiers, Tires – Scrap

Screening

Screening is the separation of a mixture of various grain sizes into two narrower size range fractions by means of a surface containing holes of a uniform size which are typically square, but other shapes of holes, particularly rectangular, are also used. The screen surface can consist of woven wire, silk or plastic cloth, perforated or punched plate, grizzly bars, or wedge wire sections. Part of the feed consisting of small enough particles can pass through the holes, and the remainder of the feedstock – consisting of larger particles – is retained on the screen surface.

However, while screening or sieving separates a mixture of solid particles according to size, the process is not always precise because the particle shape affects the size of a particle which will pass through a given size hole. Most screening operations require a size reduction operation such as crushing, grinding, or milling which produces a mixture of particulate materials that vary in size, shape, density, and abrasive properties. An initial step for such a mixture is a sieve analysis to determine the amount of the mixture that falls into the various size fractions that are relevant to the screening process.

The material passing through the screen is the *undersize* or *minus material* for the particular screen size, while the material retained on the screen is the *oversize* or *plus material*. The size distribution can be determined for the original feedstock by using a series of screens of successively smaller-sized holes. In the process, the feedstock is initially fed onto the screen having the largest holes, the undersize goes to the screen with the next largest hole size, and so on until the feed has passed through the entire series of screens. The oversize on each screen and the undersize from the smallest and final screen are weighed and reported as percentage of original feed versus screen hole size or mesh.

A standard test method (the sieve analysis test method) has been developed to determine size distributions of solid materials, and the results of the test are used to follow the effectiveness of operation of screening devices as well as the effectiveness of crushing and grinding equipment. The method uses a series of standard metal mesh sieves arranged vertically in order of increasing mesh or number of wires per inch (decreasing hole size) from top to bottom. The stack of sieves is clamped into a shaker, the feed is introduced into the top sieve, and the stack is shaken for a standardized time and intensity. The amounts left on each sieve and the final undersize are weighed and reported as percent of the feedstock.

Full-size screening operations can be used in much the same way as the above sieve analysis to fractionate a mixed feed into a group of relatively uniform-sized fractions by passing the feedstock across a series of screens having

decreasing size holes, and the oversize and undersize can be collected as desired. The full-size screens are shaken in a reciprocating, rotary, or vibrating motion as the feed passes over the screen surface, thereby providing provide a high efficiency process.

Scrubbers

Scrubber systems are a diverse group of air pollution control devices that can be used to remove particulate matter and/or gases from industrial exhaust streams. Traditionally, the term *scrubber* has referred to pollution control devices that use liquid to wash unwanted pollutants from a gas stream. Recently, the term is also used to describe systems that inject a dry reagent or slurry into a dirty exhaust stream to remove acid gases. Scrubbers are one of the primary devices that control gaseous emissions, especially acid gases. Scrubbers can also be used for heat recovery from hot gases by flue gas condensation.

A dry or semi-dry scrubbing system does not involve the use of moisture and dry scrubbers do generally not have a stack steam plume or wastewater handling/disposal requirements. Dry scrubbing systems are used to remove acid gases primarily from combustion sources.

Dry scrubbing systems can be categorized as dry sorbent injectors or as spray dryer absorbers, which are also called semi-dry scrubbers or spray dryers. Dry scrubbing systems are often used for the removal of odorous and corrosive gases from wastewater treatment plant operations. The media used is typically an activated alumina compound impregnated with materials to handle specific gases such as hydrogen sulfide.

Wet scrubbers use water to remove dust entrained in gas streams. In a wet scrubber, the polluted gas stream is brought into contact with the scrubbing liquid, by spraying it with the liquid, by forcing it through a pool of liquid, or by some other contact method, so as to remove the pollutants.

Many different types of devices are available for wet scrubbing, including spray chambers, wet cyclones, mechanical scrubbers, orifice scrubbers, venture scrubbers, and packed towers. High-energy venturi scrubbers are probably the only type that has sufficiently high removal efficiencies to satisfy emissions standards. Efficiencies between 93.6 and 99.8% have been achieved for particles smaller than 5 microns, but these efficiencies entail high pressure losses and constant gas flow rates.

Scrubbers can be designed to collect particulate matter and/or gaseous pollutants. Wet scrubbers remove dust particles by capturing them in liquid droplets. Wet scrubbers remove pollutant gases by dissolving or absorbing them into the liquid. Any droplets that are in the scrubber inlet gas must be separated from the outlet gas stream by means of another device referred to as a mist eliminator. Also, the resultant scrubbing liquid must be treated prior to any ultimate discharge or being reused in the plant.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Scrubbing

Scrubbing is a process for removing contaminants from gas streams using systems (such as chemical scrubbers, gas scrubbers) and are a diverse group of control devices that can be used to remove gases and particulate matter from gas streams. Traditionally, the term “scrubber” has referred to pollution control devices that use liquid to wash unwanted pollutants from a gas stream. Scrubbing is one of the primary processes that control gaseous emissions, especially acid gases. Scrubbers can also be used for heat recovery from hot gases by flue gas condensation.

Scrubbers can be divided into three types: (i) packed bed scrubbers, (ii) low energy scrubbers, and (iii) high energy scrubbers.

Packed bed scrubbers include countercurrent packed towers and cross-flow beds containing packings of fiber, rings, saddles, or other commercial packing materials for gas-liquid contacting. They are useful for collecting mists and soluble solids as well as absorbing gases. The low energy scrubbers include spray scrubbers, baffle- and centrifugal-type scrubbers, self-induced spray scrubbers, and some mechanically aided scrubbers. High energy scrubbers generally plate towers and many gas-atomized spray units. These latter units are venturi units or cocurrent mixers such as orifice plates or structured in-line packings. The high gas velocity relative

to the liquid in the venturi and cocurrent mixers atomizes the liquid, while the high turbulence promotes contacting of the phases. Venturi units are used mostly for dust collection only and can capture fine particles. However, they usually require a cyclone separator to remove the liquid from the treated gas and may even need further mist eliminating devices.

More specifically, a wet scrubber is used for cleaning (pollutant removal, including removal of dust particles) a gas stream. Wet scrubbing works via the contact of target compounds or particulate matter with the scrubbing solution which may be water (for dust removal) or solutions of reagents that specifically target certain compounds. Process exhaust gas can also contain water-soluble toxic and/or corrosive gases such as hydrogen chloride (HCl) or ammonia (NH_3) which can be removed by use of a wet scrubber. The removal efficiency of pollutants is improved by increasing residence time in the scrubber or by the increase of surface area of the scrubber solution by the use of a spray nozzle, packed towers, or an aspirator. However, use of a wet scrubber may increase the proportion of water in the gas, resulting in a visible stack plume, if the gas is sent to a stack. Almost all wet scrubbers involve two distinct zones of operation. In the first zone, the particles are captured and solutes are dissolved from the gas phase into the liquid. In the second zone, the liquid containing the particles and dissolved solute is removed from the gas.

A dry or semi-dry scrubbing system, unlike the wet scrubber, does not saturate the flue gas stream that is being treated with moisture. In some cases, no moisture is added, while in others, only the amount of moisture that can be evaporated in the flue gas without condensing is added. Therefore, dry scrubbers generally do not have a stack steam plume or wastewater handling/disposal requirements. Dry scrubbing systems are used to remove acid gases (such as sulfur dioxide, SO_2 and hydrogen chloride, HCl) primarily from combustion sources.

There are a number of dry type scrubbing system designs, but all consist of two main sections or devices: a device to introduce the acid gas sorbent material into the gas stream and a particulate matter control device to remove reaction products, excess sorbent material as well as any particulate matter already in the flue gas. Dry scrubbing systems can be categorized as dry sorbent injectors (DSIs) or as spray dryer adsorbers (SDAs, also called semi-dry scrubbers or spray dryers).

Dry sorbent injection involves the addition of an alkaline material [usually hydrated lime, $\text{Ca}(\text{OH})_2$, sodium carbonate, Na_2CO_3 , or sodium bicarbonate, NaHCO_3] into the gas stream to react with the acid gases. The acid gases react with the alkaline sorbents to form solid salts which are removed in the particulate control device.

In spray dryer absorbers, the flue gases are introduced into an absorbing tower (dryer) where the gases are contacted with a finely atomized alkaline slurry. Acid gases are absorbed by the slurry mixture and react to form solid salts which are removed by the particulate control device. The heat of the flue gas is used to evaporate all the water droplets, leaving a non-saturated flue gas to exit the absorber tower. Spray dryers are capable of achieving high (>80%) acid gas removal efficiencies.

See also: Gas Cleaning, Gas Processing, Gas Treating, Stripping.

Scrubbing Reagent

Alkaline sorbents are used for scrubbing flue gases to remove sulfur dioxide. Depending on the application, the two most important are lime and sodium hydroxide (caustic soda). Lime is typically used on large coal or oil-fired boilers as found in power plants, as it is very much less expensive than caustic soda. This results in the slurry being circulated through the scrubber instead of a solution and equipment performance can suffer.

A spray tower is typically used for this application. The use of lime results in a slurry of calcium sulfite (CaSO_3) that must be disposed of. Fortunately, calcium sulfite can be oxidized to produce the by-product gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which is marketable for use in the building products industry.

Caustic soda is limited to smaller combustion units because it is more expensive than lime, but it has the advantage that it forms a solution rather than a slurry. This makes it easier to operate. It produces a solution of sodium sulfite/bisulfite (depending on the pH), or sodium sulfate that must be sent to disposal.

It is possible to remove sulfur dioxide by using a cold solution of sodium sulfite, which forms a sodium hydrogen sulfite solution. By heating this solution, the reaction can be reversed to form sulfur dioxide and the sodium sulfite solution. In theory, the sodium sulfite does not undergo a chemical change during the extraction from water to another phase. While a chemical change does occur during the extraction of the sulfur dioxide from the gas mixture,

it is the case that the extraction equilibrium is shifted by changing the temperature rather than by the use of a chemical reagent.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Seashore Mallow

Many land areas are presently not arable because freshwater is lacking, the soils are naturally saline, or the soils are salty as the result of previous agricultural practices. Many of these areas have abundant saline water available either as surface or ground water. Seashore mallow is a novel salt-tolerant perennial crop, derived from a salt marsh plant. With an oil content of approximately 18% w/w and residual meal that contains 30% w/w protein, this crop can be grown on saline land and produce vegetable oil on underutilized or non-arable land.

Seashore mallow has a productive life of approximately ten years, and the oil is similar in fatty acid composition to the oil from cottonseed. There are few reported insects or diseases that impact the crop; breeding efforts have been almost non-existent. Due to limited breeding efforts, the yields of seashore mallow are low compared to other oilseeds. Researchers envision at least four ways that the seashore mallow may fit into agronomic scenarios: (i) grown on salinized farmland, (ii) grown on dry farmland with brackish water wells, (iii) grown on sandy coastal deserts, or (iv) grown on farmland or aquatic ecosystems in transition.

Secondary Biomass Feedstocks

Biomass is a renewable energy source derived from living, or recently living organisms, such as wood, waste, and alcohol fuels. For example, forest residues (such as dead trees, branches, and tree stumps), yard clippings and wood chips, and garbage may be used as biomass.

Secondary biomass feedstocks differ from primary biomass feedstocks in that the secondary feedstocks are a by-product of processing of the primary feedstocks. By processing, it is meant that there is substantial physical or chemical breakdown of the primary biomass and production of by-products; processors may be factories or animals. Field processes such as harvesting, bundling, chipping, or pressing do not cause a biomass resource that was produced by photosynthesis (e.g., tree tops and limbs) to be classified as secondary biomass.

Specific examples of secondary biomass include sawdust from sawmills, black liquor (which is a by-product of paper making), and cheese whey (which is a by-product of cheese making processes). Manure from concentrated animal feeding operations is collectable secondary biomass resources. Vegetable oils used for biodiesel that are derived directly from the processing of oilseeds for various uses are also a secondary biomass resource.

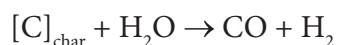
Residues and by-product streams from food, feed, fiber, wood, and materials processing plants are the main source of secondary biomass. Secondary biomass feedstocks differ from primary biomass feedstocks in that the secondary feedstocks are a by-product of processing of the primary feedstocks.

By processing, it is meant that there is substantial physical or chemical breakdown of the primary biomass and production of by-products. Processors may be factories or animals. Field processes such as harvesting, bundling, chipping, or pressing do not cause a biomass resource that was produced by photosynthesis (e.g., tree tops and limbs) to be classified as secondary biomass.

See also: Biomass, Primary Biomass.

Secondary Gasification

Secondary gasification typically involves the gasification of char from the primary gasifier. This is usually accomplished by reacting the hot char with water vapor to produce carbon monoxide and hydrogen:



See also: Biomass Gasification, Gasification.

Sedimentation

Sedimentation is a physical process where particles suspended in a liquid are forced to settle by a combination of gravity and inertial forces on both the solid particles and the liquid carrier. In order to achieve sedimentation, the net forces on a particle in the desired direction of settling must be greater than the forces tending to move the particle in the opposite direction. This net force causes the particle to move in the desired direction which would be upward for low density particles which float in water, or downward for high density particles such as the metal hydroxides and sulfides.

In the current context, sedimentation is the tendency for chemicals in suspension in water to settle out of the water and come to rest against a barrier. In geology, sedimentation is often used as the opposite of erosion, i.e., the terminal end of sediment transport. Settling is the falling of suspended particles through the liquid, whereas sedimentation is the termination of the settling process. Sedimentation may pertain to objects of various sizes, ranging from large rocks in flowing water to suspensions of dust which produce significant sedimentation. The term is typically used in geology to describe the deposition of sediment which results in the formation of sedimentary rock.

Sedimentation can be achieved in either batch or continuous equipment. However, continuous equipment is much more common, especially where large volumes of wastewater are to be treated. In recent years, a number of manufacturers have developed compact, continuous units for the entire pretreatment of wastewater. These units provide first chemical precipitation and pH adjustment and then sedimentation and clarification of the resulting slurry.

Sedimentation can be generally classified into three different types that are all applicable to chemicals. Type 1 sedimentation is characterized by particles that settle discretely at a constant settling velocity, and typically, these particles settle as individual particles and do not flocculate or stick to other during settling. Type 2 sedimentation is characterized by particles that flocculate during sedimentation, and because of this, the particle size is constantly changing, and therefore their settling velocity is changing. Type 3 sedimentation (also known as zone sedimentation) involves particles that are at a high concentration (for example, greater than 1,000 mg/L) such that the particles tend to settle as a mass and a distinct clear zone and sludge zone are present. Zone settling occurs in active sludge sedimentation and sedimentation of sludge thickeners.

In terms of the sedimentation of chemicals, some of the chemicals may be adsorbed on the suspended material (especially if the suspended material is clay or another highly adsorptive mineral) and deposited to the bottom. This mainly happens in shallow waters where particulate matter is abundant and water is subjected to intense mixing, usually through turbulence. Simultaneously, the process of biosedimentation can also occur when plankton and other organisms absorb the chemical. The suspended forms of the chemicals undergo intense chemical and biological (microbial) decomposition in the water. However, this situation radically changes when the suspended chemical reaches the lake bed, river bed, or sea bed and the decomposition rate of the chemical(s) buried on the bottom abruptly drops. The oxidation processes slow down, especially under anaerobic conditions in the bottom environment, and the chemical(s) accumulated inside the sediments can be preserved for many months and even years.

Flocculation and coagulation agents are commonly used in conjunction with sedimentation in aqueous systems to improve the separation of the precipitated solids (or sludge) from the aqueous phase. Coagulation is the collection or aggregation of small colloidal particles of precipitate to form larger aggregate particles. Coagulation is enhanced by the addition of strongly ionic chemicals such as acids, lime, alum, or ferrous sulfate in a region of intense mixing. Flocculation is the further growth of the coagulated aggregates by their coalescence as the aggregates contact one another. Flocculation is a slower process than coagulation but produces larger, more easily settled particles.

See also: Chemical Precipitation, Coagulation, Flocculation.

Sedimentary Strata

By definition, a rock is any naturally formed, nonliving, coherent aggregate mass of solid matter that constitutes part of a planet, asteroid, moon, or other planetary object. There are three families of rocks: (i) igneous rocks, which are formed from the cooling and consolidation of magma or lava, (ii) sedimentary rocks, which are formed from either chemical precipitation of material or deposition of particles transported in suspension, and (iii) metamorphic rocks,

which are formed from changing a rock as a result of high temperatures, high pressures, or both. It is the second of the three types of rock to which this section is devoted.

The sedimentary rock is typically from as a stratum (or layer) that was deposited over time because of a physical or chemical effect that caused the rock to form particles that then deposited in the layer. A sequence of strata (pl: layers) deposited without interruption is said to be *conformable*, but if there are breaks in the strata that represent times of non-deposition or erosion, the term to be applied is *unconformity*.

Stratification is the layering that occurs in most sedimentary rocks and at the surface of the Earth, typically from fragmental deposits. The layers can range from fractions of an inch to several feet (or even to several yards) in thickness and vary in shape. The strata may range from thin sheets that cover many square miles to thick lens-like bodies that extend (laterally) only a few feet.

Stratigraphy is the branch of geology that focuses on the study of strata (rock layers) and layering (stratification). Stratigraphy has two related subfields: (i) lithostratigraphy (lithologic stratigraphy) and biostratigraphy (biologic stratigraphy). The former (lithostratigraphy) focuses on the variation in rock units, most obviously displayed as visible layering, due to physical contrasts in rock type (lithology) which can occur vertically as layering (bedding), or laterally, and reflects changes in the environments of the deposition (facies change). These variations provide a lithostratigraphy or lithologic stratigraphy of the rock unit.

See also: Sedimentation.

Selectox Process

Liquid redox sulfur recovery processes are liquid-phase oxidation processes which use a dilute aqueous solution of iron or vanadium to remove hydrogen sulfide selectively by chemical absorption from sour gas streams. These processes can be used on relatively small or dilute hydrogen sulfide stream to recover sulfur from the acid gas stream, or, in some cases, they can be used in place of an acid gas removal process. The mildly alkaline lean liquid scrubs the hydrogen sulfide from the inlet gas stream, and the catalyst oxidizes the hydrogen sulfide to elemental sulfur. The reduced catalyst is regenerated by contact with air in the oxidizer(s). Sulfur is removed from the solution by flotation or settling, depending on the process.

The *Selectox process* is based on replacing the Claus first stage thermal reactor (the furnace) with a catalytic oxidation step. A catalytic oxidation reactor can operate at much lower temperatures than the furnace and maintain a more stable flame temperature with lean hydrogen sulfide feeds.

Two versions of the process are offered. The first option is a once-through option, treating acid gases with up to 5% hydrogen sulfide and in which sulfur recovery is on the order of 84 to 94% w/w for hydrogen sulfide in the feed gas of 2 to 5% v/v, respectively. In the second option, which is a recycle version that handles hydrogen sulfide concentrations on the order of 5 to 100% v/v, the gas is recycled from the Selectox reactor condenser to cool the reactor outlet temperature not to exceed 370°C (700°F). The temperature limit is set so that carbon steel can be used for the reactor vessel.

The recycle Selectox process is an all-catalytic process in which there are no flames at any point in the process. A special catalyst bed replaces the acid gas burner in a conventional Claus plant, and the catalyst occupies the top few inches of the first bed, where it promotes the selective oxidation of hydrogen sulfide to sulfur dioxide. The remainder of the bed is filled with Claus catalyst where the Claus reaction occurs to approximately 80% completion. The highly exothermic nature of these reactions requires that the feed gas be monitored for the concentration of hydrogen sulfide to avoid overheating.

Approximately 80% v/v of the hydrogen sulfide is converted to sulfur in the Selectox reactor. The reactions are of the typical Claus type: the first reaction is the conversion of hydrogen sulfide to sulfur dioxide as the predominant reaction, then the hydrogen sulfide reacts with the sulfur dioxide to form elemental sulfur. The rest of the sulfur is recovered in conventional Claus stages. Up to 98% w/w sulfur recovery efficiency can be achieved for a 50% hydrogen sulfide acid gas feed to the recycle version of the Selectox process. Higher sulfur recoveries can only be had with tail gas treating, such as the BSR/Selectox process.

In the BSR/Selectox tail gas process, the gases are first hydrogenated to hydrogen sulfide in the Beavon Stretford Reactor (BSR), then they proceed to another Selectox reactor stage. Sulfur recoveries up to 99.3% w/w have been reported for BSR/Selectox.

See also: Claus Process, Gas Cleaning, Gas Processing, Gas Treating, SCOT Process.

Selexol Process

The Selexol process (unlike amine-based acid gas removal solvents that rely on a chemical reaction with the acid gases) uses a physical solvent made of dimethyl ethers of polyethylene glycol (DEPG, the Selexol solvent), to selectively remove hydrogen sulfide (H_2S) and carbonyl sulfide (COS) plus carbon dioxide (CO_2) in bulk from gas streams. The process is also effective for the removal of (and control of) mercaptan sulfur (RSH).

The process solvent (which is a widely used physical solvent process for gas cleaning) is a mixture of dimethyl ethers of polyethylene glycol $[\text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3]$ where n is between 3 and 9. The solvent is chemically and thermally stable, and has a low vapor pressure that limits its losses to the treated gas. The solvent has a high solubility for carbon dioxide, hydrogen sulfide, and carbonyl sulfide. It also has appreciable selectivity for hydrogen sulfide over carbon dioxide.

As with all physical solvent processes, the principal benefits are (i) high selectivity for hydrogen sulfide over carbonyl sulfide and carbon dioxide, (ii) high loadings at high acid gas partial pressures, (iii) solvent stability, and (iv) low heat requirements because most of the solvent can be regenerated by pressure letdown.

The Selexol process can be configured in various ways, depending on the requirements for the level of hydrogen sulfide/carbon dioxide selectivity, the depth of sulfur removal, the need for bulk carbon dioxide removal, and whether the gas needs to be dehydrated. The gas stream from the low-pressure flash is combined with the acid gas from the regenerator. This combined gas stream is then sent to a sulfur recovery unit. However, the hydrogen sulfide content could be too low for use in a conventional Claus plant. The process can also be configured to give both a rich acid gas feed to the Claus unit as well as to provide for bulk carbon dioxide removal.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Separation Processes – Definition and Characteristics

A separation process is any process that is designed to separate the products from the feedstock or to separate different products from each other or any combination of these two options.

A large number of different separation processes exist which are based on different techniques to generate a composition difference between the products of a process and the different processes into types defined by (i) the nature of the feedstock, (ii) the method of generating concentration differences, and (iii) whether or not the separation depended on the addition of special separating agents as well as energy.

Heterogeneous feedstocks contain more than one phase of matter (i.e., gas, liquid, or solid) and can contain almost any combination of gas liquid, liquid, or solid in a gas, liquid, or solid matrix. The exception is gas in gas systems, which are generally homogeneous except for some circumstances where a gas mixture very special mixtures which separate into two gaseous phases at high pressure. Many of the feedstocks encountered in alternative energy systems may be the heterogeneous type. Typical examples are slurries of solids, sludge, dusts, and mists in the products from manufacturing processes or incinerators; mixtures of solid phases encountered in ore processing or solid waste handling; and emulsions from metalworking plants. These types of feedstocks are separated by mechanical separation processes such as settling, centrifugation, flotation, filtration, magnetic separation, and electrostatic precipitation.

On the other hand, relatively simple mechanical equipment is needed to separate heterogeneous feedstocks into their individual phases; however, homogeneous feedstocks typically require a diffusional transfer of matter to one of the product streams. These processes generate two phases of different composition from the feedstock and then separate the phases to give two products of composition different from both the feedstock and each other. In some cases, the product phases may be in equilibrium when they are generated, as in simple distillation. Alternatively, the phases may be thoroughly mixed with one another to achieve equilibrium prior to phase separation. Examples of such equilibrium processes are distillation, extraction, adsorption, ion exchange, crystallization, and evaporation.

Unlike the equilibrium processes, some separation processes get the impetus from a gradient of temperature, pressure, and composition and achieve a change in composition of the product from differences in diffusion rate of

feed components through a barrier across which the gradient is applied. Processes of this type (typically referred to as rate-controlled processes) are illustrated by (i) membrane processes such as gaseous diffusion, ultrafiltration, reverse osmosis, and permeation, and (ii) processes depending on slow chemical reactions to make the separation, as in some carbon dioxide scrubbing processes that are designed to remove, say, carbon dioxide from a gas stream.

See also: Recovery Processes.

Separation Processes – Separation of Solids

The processes for separating various types of solid materials from each other are much different from the equilibrium processes used to separate liquids and gases. The processes for solids make use of physical differences in either a bulk property of the solids or in a surface property of the solids. Thus, the processes are more dependent on physical characteristics rather than on chemical characteristics and are essentially sorting processes.

A sorting process is a process that involves placing the components of a mixture into a specific place which involves separation of the mixture (of solid materials) into homogeneous groups according to the characteristics of the individual components. Typical examples of sorting processes in waste management are (i) the separation of glass, plastic, paper, and metals from each other, (ii) the separation of glass bottles into brown, green, and clear glass categories, (iii) the separation of plastic containers according to the type of polymer used in their manufacture, and (iv) separation of scrap metals or metal cans into ferrous and non-ferrous categories. These types of sorting processes are essential to permit effective recycling programs to be achieved, and the products of the process must not be cross-contaminated and must be homogeneous enough to be used as raw material in a manufacturing process.

For example, a sorting process (or sorting program) may involve the following steps: (i) the recyclable waste is placed on a presorting floor where paper materials – such as newspapers – and non-recyclable materials are removed. The remaining material is then put on conveyer belts and fed consecutively through separation devices which remove different materials and put them in separate bins for recycling.

For example, magnetic separation removes tramp iron and steel cans, while screening to remove fines eliminates sand and broken glass. Either air blowing or the chain curtain sorting machine is used to separate light aluminum and plastic containers from glass bottles and jars, after which the glass is then sorted by color either automatically or by hand. The large plastic bottles are removed by coarse screening, and the aluminum cans are removed by an eddy current magnetic separator. Finally, the plastic is separated by polymer type either manually or automatically.

The bulk properties typically chosen as a basis for sorting solids are size, density, magnetic permeability, or electrical conductivity. Solids are sorted by size over a wide size range using screens and rotating perforated drums. A combination of size and density controls the separation of solids in jigs and tables for larger sizes and in fluid beds or by elutriation for smaller sizes. The separation of solids according to density alone is usually achieved using a cyclone separator for small sizes and in cones and rotating drums for larger sizes.

A difference in the magnetic permeability between different solids is the basis for magnetic separation of many metals and mineral ores. It is also the basis for the separation of steel cans and steel scrap from trash. Finally, differences in the electrical conductivity of different solids make it possible to separate them using electrostatic forces. For example, insulating materials are slow to accept electrical charge but hold it well once charged. On the other hand, electrical conductors charge rapidly but also lose their charge rapidly. The surface properties of solids most frequently used as a basis for a separation process are surface tension, wettability, color, surface conductivity, and reflectance. Surface tension and wettability are the basis for separation of fine solids by flotation.

Processes for separation of solids by type of material can be divided into two major classes: (i) use of the properties of the solid to provide the force to do the separation, which includes magnetic separation processes, electrostatic separation, screening processes, and flotation processes, and (ii) automatic sorting which depends on monitoring a flowing stream of solids with a suitable detector which can distinguish between the types of solids to be separated – when the detector senses a material which is not of the desired type, it activates a mechanical device which removes that material from the flowing stream.

See also: Advanced Cycloning, Centrifugal Separation, Cyclone Separation, Recovery Processes, Screening, Settling and Flotation, Waste, Waste Management.

Settling and Flotation

Gravity settling is a commonly used process for separating insoluble particles of solids or liquids from a liquid or gaseous carrier fluid and the process involves the use of the effect of gravity on the difference in density between the dispersed particles and the carrier fluid in which the particles are dispersed. If the particles are more dense (heavier) than the carrier fluid, they sink to the bottom of the settling chamber. If the particles are less dense (lighter) than the carrier fluid, they rise to the surface of the liquid.

Gravity settling is a subcategory of the more general field of sedimentation, which includes the slower processes of hindered settling, flocculation, coagulation, clarification, and thickening.

Furthermore, gravity separation can be enhanced by the use of centrifuges and cyclones.

Flotation is also a gravity separation to remove insoluble particles from a liquid. However, it uses bubbles of gas, usually air, that attach to the insoluble particles and lift them to the surface of the liquid by buoyancy. The particles can then be removed from the surface by various skimming devices. By selectively attaching the bubbles to one particular kind of particle in a mixture, separation can be made between particles lifted to the surface and particles settled to the bottom.

See also: Centrifugal Separation, Cyclone Separation See also: Recovery Processes.

Shell Gasification Process

The Shell gasification (partial oxidation) process is a flexible process for generating synthesis gas, principally hydrogen and carbon monoxide, for the ultimate production of high-purity high pressure hydrogen, ammonia, methanol, fuel gas, town gas or reducing gas by reaction of gaseous or liquid hydrocarbon derivatives with oxygen, air, or oxygen-enriched air. The most important step in converting the feedstock to industrial gas is the partial oxidation of the oil using oxygen with the addition of steam. The gasification process takes place in an empty, refractory-lined reactor at temperatures on the order of 1,400°C (2,550°F) and pressures between 29 to 1140 psi.

The chemical reactions in the gasification reactor proceed without catalyst to produce gas containing carbon amounting to some 0.5 to 2% by weight, based on the feedstock. The carbon is removed from the gas with water, extracted in most cases with feed oil from the water and returned to the feed oil. The high reformed gas temperature is utilized in a waste heat boiler for generating steam. The steam is generated at 850 to 1,565 psi. Some of the steam is used as process steam and for oxygen and oil preheating. The surplus steam is used for energy production and heating purposes.

See also: Gasification, Gasifiers.

Shell Gasifier

The Shell gasifier uses a pressurized, slagging entrained flow reactor for gasifying dry pulverized coal and has the potential to gasify a wide range of feedstocks. Unlike other gasifying systems, it uses pure oxygen as the gasifying medium.

In the process, the feedstock coal, before feeding to the gasifier vessel, is crushed and ground to a size less than 90 mm after which it is fed through diametrically opposite diffuser guns into the reaction chamber. The feedstock is then reacted with the pure oxygen and steam where the flame temperature reaches as high as 1,800 to 2,000°C at approximately 450 psi.

The raw product gas typically consists mainly of carbon monoxide and hydrogen with some quantities of carbon dioxide and nitrogen. A water-filled bottom compartment is provided where molten ash is collected. A quench section is provided at the reactor outlet. Removal of particulate matter from the raw gas is integrated with the overall process. This removal system consists of cyclones and scrubbers.

See also: Gasification, Gasifiers.

Shell-Paques Process

The Shell-Paques process for biological gas desulfurization integrates gas purification with sulphur recovery in one process unit. Hydrogen sulfide removal efficiencies greater than 99.8% can be reliably achieved, and treated gas can contain less than 4 ppm of hydrogen sulfide. The process is ideally suited to environmentally sensitive locations where flaring, incineration, or other combustion options are undesirable. Its application range is from 0.1 to 50 t/d of sulfur per unit.

In the process, a gas stream containing hydrogen sulfide contacts an aqueous soda solution containing sulfur bacteria in an absorber. The soda absorbs the hydrogen sulfide and is then transferred to a regenerator consisting of an aerated atmospheric tank where hydrogen sulfide is biologically converted to elemental sulfur. Sulfur may be recovered as a moist filter cake or as pure liquid sulfur.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Shell-Paques/Thiopaq Process

The Shell-Paques/THIOPAQ is a biological process for removing hydrogen sulfide from (high-pressure) natural gas, synthesis gas and refinery gas streams.

In this process, essentially complete removal of hydrogen sulfide can be achieved by selective biological conversion of hydrogen sulfide into elemental sulfur.

In comparison with conventional liquid redox processes significant savings in capital and especially operating costs can be achieved. In addition, economic savings can be delivered compared to conventional amine + Claus + SCOT technology for loadings of up to 50 ton sulfur/day; this upper limit increases continuously due to optimization of the process.

The sulfur produced has a hydrophilic nature, which significantly reduces the chance of equipment fouling or blocking. Moreover, this characteristic makes the product suitable for agricultural use as fertilizer. Alternatively, the sulfur can be melted to yield a high purity product which meets international Claus sulfur specifications.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Shell SGP Process

The Shell gasification process consists of three principal stages: (i) gasification, sometimes referred to as partial oxidation, in which the feedstock is converted to synthesis gas (syngas) in the presence of oxygen and a moderating agent (steam) in a refractory-lined gasification reactor, (ii) synthesis gas effluent cooler in which high pressure steam is generated from the hot synthesis gas leaving the reactor, and (iii) carbon removal, in which residual carbon and ash are removed from the synthesis gas in a two-stage water scrubbing unit. The final stage involves a soot water processing section, naphtha soot recycling unit (NSRU), or soot ash removal unit (SARU), which recovers carbon from the wash water and separates the metal ash from the carbon to yield a valuable product.

Both the feedstock and the gasification agent, oxygen, are preheated prior to being fed to the burner which is a proprietary co-annular burner specially designed for viscous feedstocks.

The partial oxidation reaction takes place at approximately 1,300 to 1,400°C (2,370 to 2,550°F) in the refractory-lined reactor. The sensible heat of the hot gas is used to generate high-pressure steam, with or without superheat as required. The non-catalytic partial oxidation reactor produces small amounts of soot that are washed out in a scrubber. The carbon is concentrated in the reaction water that is discharged to the wastewater treatment.

See also: Fischer Tropsch, Gasification, Synthesis Gas.

Shell SMDS Process

The Shell middle distillate synthesis (SMDS) process is a three-stage process that involves the Fischer-Tropsch synthesis of paraffinic wax called the high-boiling paraffin synthesis.

In the first stage synthesis, gas is obtained by partial oxidation of natural gas with pure oxygen in the Shell gasification process. In the second stage, high-boiling (high-molecular-weight) paraffin synthesis, the synthesis gas is converted into liquid hydrocarbon derivatives. In the third and final stage, the waxy syncrude is fractionated into high-quality products, a part of which is converted into middle distillates by means of the high-boiling paraffin (high-molecular-weight paraffin) conversion.

The heart of the process is an enhanced Fischer-Tropsch process. However, direct Fischer-Tropsch synthesis does not allow the selective production of materials of narrow carbon number range. To overcome this limitation, the flexible two-stage concept of SMDS combines the chain-length-independent Fischer-Tropsch chain-growth reaction with a chain-length-dependent cracking process. Naphtha, kerosene, and gas oil yield ratios can be varied from 15:25:60 to 25:50:25. Both the kerosene and gas oil show excellent combustion properties: the smoke point of the kerosene can be over 45 mm, and the gas oil has a cetane number in excess of 70.

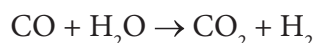
The wax (high-molecular-weight paraffin) is subsequently hydrocracked and isomerized (in the presence of hydrogen) to yield a middle distillate boiling range product in the high-boiling paraffin conversion. In the high-boiling paraffin synthesis stage, wax is maximized by using a proprietary catalyst having high selectivity toward higher-boiling products and by the use of a tubular, fixed-bed reactor. The high-boiling paraffin conversion high-boiling paraffin conversion stage employs a commercial hydrocracking catalyst in a trickle flow reactor. The high-boiling paraffin conversion step allows for production of narrow range hydrocarbon derivatives not possible with conventional Fischer-Tropsch technology.

The products manufactured are predominantly paraffinic, free from sulfur, nitrogen, and other impurities, and have excellent combustion properties. The high cetane number and smoke point indicate clean-burning hydrocarbon liquids having reduced harmful exhaust emissions. The process can also be proposed to produce chemical intermediates, paraffinic solvents, and extra high viscosity index lube oils.

See also: Fischer Tropsch, Synthesis Gas.

Shift Conversion

The second important reaction in a steam reforming plant is the shift conversion reaction:



Two basic types of shift catalyst are used in steam reforming plants: iron/chrome high temperature shift catalysts, and copper/zinc low temperature shift catalysts.

High-temperature shift catalysts operate in the range of 315 to 430°C (600 to 800°F) and consist primarily of magnetite (Fe_3O_4) with trivalent chromium oxide (Cr_2O_3) added as a stabilizer. The catalyst is usually supplied in the form of ferric oxide (Fe_2O_3) and six-valent chromium oxide (CrO_3) and is reduced by the hydrogen and carbon monoxide in the shift feed gas as part of the start-up procedure to produce the catalyst in the desired form. However, caution is necessary since if the steam/carbon ratio of the feedstock is too low and the reducing environment too strong; the catalyst can be reduced further, to metallic iron. Metallic iron is a catalyst for Fischer-Tropsch reactions, and hydrocarbon derivatives will be produced.

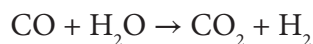
Low-temperature shift catalysts operate at temperatures on the order of 205 to 230°C (400 to 450°F). Because of the lower temperature, the reaction equilibrium is more controllable and lower amounts of carbon monoxide are produced. The low-temperature shift catalyst is primarily used in wet scrubbing plants that use methanation for final purification. Pressure swing adsorption plants do not generally use a low-temperature because since any unconverted carbon monoxide is recovered as reformer fuel. Low-temperature shift catalysts are sensitive to poisoning by sulfur and are sensitive to water (liquid) that can cause softening of the catalyst followed by crusting or plugging.

The catalyst is supplied as copper oxide (CuO) on a zinc oxide (ZnO) carrier, and the copper must be reduced by heating it in a stream of inert gas with measured quantities of hydrogen. The reduction of the copper oxide is strongly exothermic and must be closely monitored.

See also: Gasification Chemistry.

Shift Conversion Catalysts

The second important reaction in a steam reforming plant is the shift conversion reaction:



Two basic types of shift catalyst are used in steam reforming plants: iron/chrome high temperature shift catalysts, and copper/zinc low temperature shift catalysts.

High-temperature shift catalysts operate in the range of 315 to 430°C (600 to 800°F) and consist primarily of magnetite (Fe_3O_4) with three-valent chromium oxide (Cr_2O_3) added as a stabilizer. The catalyst is usually supplied in the form of ferric oxide (Fe_2O_3) and six-valent chromium oxide (CrO_3) and is reduced by the hydrogen and carbon monoxide in the shift feed gas as part of the start-up procedure to produce the catalyst in the desired form. However, caution is necessary since if the steam/carbon ratio of the feedstock is too low and the reducing environment too strong, the catalyst can be reduced further, to metallic iron. Metallic iron is a catalyst for Fischer-Tropsch reactions, and hydrocarbon derivatives will be produced.

Low-temperature shift catalysts operate at temperatures on the order of 205 to 230°C (400 to 450°F). Because of the lower temperature, the reaction equilibrium is more controllable and lower amounts of carbon monoxide are produced. The low-temperature shift catalyst is primarily used in wet scrubbing plants that use methanation for final purification. Pressure swing adsorption plants do not generally use a low-temperature catalyst because since any unconverted carbon monoxide is recovered as reformer fuel. Low-temperature shift catalysts are sensitive to poisoning by sulfur and are sensitive to water (liquid) that can cause softening of the catalyst followed by crusting or plugging.

The catalyst is supplied as copper oxide (CuO) on a zinc oxide (ZnO) carrier, and the copper must be reduced by heating it in a stream of inert gas with measured quantities of hydrogen. The reduction of the copper oxide is strongly exothermic and must be closely monitored.

See also: Gasification Chemistry.

Short Rotation Coppice

Short rotation coppice (SRC, or short rotation woody crops) refers to fast-growing deciduous trees which are grown as energy crops, such as willow and poplar trees. The species of short rotation coppice that are most suitable, and therefore most popular, for use as energy crops are poplar and willow (and possibly also birch) because they both require deep, moisture-retentive soils for proper growth. Willow, in particular, is able to endure periods of water logging and is therefore better suited to wetter soil.

Short rotation coppice is harvested on a 2-to-5-year cycle, although commonly every 3 years. Willow and poplar are adapted to cool climates and tolerate temporary wet conditions better than most of other species.

The harvesting of the wood takes place at the vegetative rest during the winter months. At this time of the year, the wood has a water content of around 50 %. Harvesting can be carried out using three main methods which are (i) the coppice is cut and bundled in bundles, (ii) the coppice is cut and chipped in a single operation, then blown into a trailer, and (iii) an intermediate system where the coppice is cut into billets and blown into a trailer. After harvesting, the product may be stored for a few weeks in order to reduce its moisture content to a satisfactory level for use in energy production. Dry short rotation coppice can then be burnt under controlled conditions to produce other fuels, gas or liquid, which are then used for electricity generation.

A plantation could be viable for up to 30 years before re-planting becomes necessary, although the yield decreases after 5-6 rotations.

Short rotation coppice (SRC) (such as willow and poplar) is densely planted, high-yielding varieties. It is harvested on a 2-to-5-year cycle, although commonly every 3 years. Willow and poplar are adapted to cool climates and tolerate temporary wet conditions better than most of other species. The harvesting of the wood takes place at the vegetative rest (November to February). At this time of the year, the wood has a water content of around 50%. Performance of short rotation coppice depends on the selection of species, environmental conditions, fertilizers, soil, etc. and can reach up to 20 t/ha. However, usually, yield ranges from 5 to 15 t/ha of dry matter. Harvesting can

be carried out using 3 main methods: the coppice is cut and bundled in bundles; the coppice is cut and chipped in a single operation, then blown into a trailer; and an intermediate system where the coppice is cut into billets and blown into a trailer. Performance of short rotation coppice can be harvested with chopper machinery, called a chopper harvester. But conventional machineries are not really adapted for harvesting.

The species of short rotation coppice that are most suitable, and therefore most popular, for use as energy crops are poplar and willow (and possibly also birch) because they both require deep, moisture-retentive soils for proper growth. Willow, in particular, is able to endure periods of water logging and is therefore better suited to wetter soils. Short rotation coppice is harvested during winter when the dry matter percentage of the coppice is at its highest, and it is then bundled or immediately chipped. It may then be stored for a few weeks in order to reduce its moisture content to a satisfactory level for use in energy production. Dry short rotation coppice can then be burnt under controlled conditions to produce other fuels, gas or liquid, which are then used for electricity generation.

See also: Short Rotational Coppicing, Biomass, Wood.

Short Rotational Coppicing

Short rotational arable coppicing is currently viewed by some as a potentially important source of fuel for electricity generation.

Crops tend to be established by planting cuttings in cultivated ground. Coppicing occurs every 2 to 4 years when stems are harvested by cutting 3 to 4 inches above ground level (cutting cycle). Cutting cycles can vary depending on the objectives of management and available land.

Energy crops include (i) willows, (ii) poplars, (iii) hemp, (iv) miscanthus, which is a temperate climate grass adapted to moist soils and sewage sludge can be used as fertilizer for this plant, (v) maize, and (vi) sorghum, which is a grass-like grain crop that produces sugars.

Willow has been the main tree species highlighted for short rotational coppicing – poplar may also be used and produces large amounts of biomass in relatively short periods due to its fast-growing nature. In addition, willow will thrive in a wide range of soil types and can be grown from cuttings, provided there is an adequate water supply (and as far as “sunny” Scotland is concerned, this does not pose a problem). Care needs to be taken to control weeds and protect new plantations from rabbits and deer. During growth, the use of fertilizers and chemicals is lower than for most agricultural crops. The willow can be cut back at the end of the first year as this encourages growth of multiple shoots; alternatively, plantations could be removed and the land returned to agricultural crops if things are not going as planned. Yields from coppicing can be stored until needed and then used to generate heat and electricity.

See also: Short Rotational Coppice; Wood.

Short Rotation Forestry

The dedicated cultivation of short-rotation (over a total period of 3 to 30 years) wood species is recently getting an increasing popularity in Europe. Willow (*Salix*) and to a lesser extent – poplar (*Populus*) are the favorite species.

Willow is harvested in 2-to-4-year intervals, when the shoots are approximately of 20 feet of height, normally in the winter in order to reduce the moisture content. After harvesting, willow stumps are left to coppice and another crop grows in 2 to 4 years. Poplar needs longer harvest intervals – 8 to 15 years.

Achieving high yields is only possible under specific cultivation conditions. For instance, poplar and especially willow require substantial quantities of water, i.e., the growth rate is reduced in dry conditions or dry years. The cultivation of short rotation forestry could also result in groundwater depletion. Nevertheless, planting perennial short rotation forestry brings some clear environmental benefits, compared to growing conventional annual crops – less soil disturbance and more soil cover (leading to reduced soil erosion), lower fertilizer, and pesticide inputs.

The cultivation and harvesting of short rotation forestry is also very energy-efficient since it consumes little energy – only 4 to 5% of the energy content of the harvested material. The core drawback of dedicated woody crops is the much higher cost compared to various wood residues from thinning as well as the pulp and paper industry.

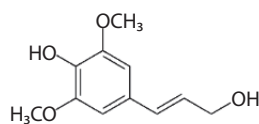
Hence, the reduction of cultivation costs of short rotation forestry is a main challenge and prerequisite for its larger utilization.

Another drawback of woody crops is the typically high moisture content that is not appropriate for the gasification process. Thus, the woody feedstock from short rotation forestry typically requires pre-drying.

See also: Biomass, Gasification, Wood, Wood Biomass.

Sinapyl Alcohol

Sinapyl alcohol is an organic compound structurally related to cinnamic acid. It is biosynthesized via the phenylpropanoid biochemical pathway, its immediate precursor being sinapaldehyde. This phytochemical is one of the monolignols, which are precursor to lignin or lignans.



Sinapyl alcohol

Sinapyl alcohol is slightly soluble (in water) and is a very weakly acidic compound.

See also: Coniferyl Alcohol, Lignin, Paracoumaryl Alcohol.

Sizing

Sizing of the feedstock may be necessary as different sizes are specified for different types of gasifiers. For small-scale fixed bed gasifiers, cutting and/or sawing of wood blocks is the preferred form of fuel preparation. Chipped wood is preferred for larger scale applications. The size range of chips can be chosen by screening such that the fuel is acceptable for a specific gasifier type. For medium- and large-scale fixed bed gasifiers, wood chips from forestry or wood processing industries are produced by crushers, hammer mills, shredders, and/or mobile chippers (particularly for thinnings from landscape conservation activities). Most of these sizing apparatus are provided with a screen. Dependent on the feedstock morphology and characteristics (hardness), the throughput or capacity varies considerably.

See also: Gasification.

Slagging, Fouling, and Clinkering

Slagging is the accumulation of ash on the wall tubes of a boiler furnace, forming a solid layer of ash residue and interfering with heat transfer. It is the fused or resolidified molten materials that form primarily on furnace walls or other surfaces. Slag usually forms at locations where temperatures are high. Changes to slagging potential affect furnace sizing, arrangement of radiant and convective heating surfaces, and the number of soot blowers required.

During combustion, there are zones in which the supply of oxygen is depleted or carbon dioxide is reversibly reduced to carbon monoxide in the presence of excess carbon. This can produce a reducing atmosphere in a hot zone where ash particles in an incipient state of fusion begin to melt. The significance of performing the test in reducing and oxidizing atmospheres is that most oxides of metals exhibit higher fusion temperatures in their highest state of oxidation.

The critical temperature most commonly referenced in the evaluation of the properties of ash is the softening temperature. This is the temperature at which the cone has fused down to a spherical lump in which the height is equal to the width at the base.

Slagging Lurgi Gasifier

The major disadvantage of the dry ash Lurgi gasifier is that temperatures have to be maintained below the ash melting point to prevent clinking. As a consequence, steam utilization is poor and efficiencies are relatively low. Moreover, low reactivity coals are of concern since they require higher steam/oxygen ratios to hold down the temperature. To improve the performance of the gasifier—and in line with the current leaning toward high temperature operation for increased reaction rates, higher steam utilization, and reduced methane formation—a slagging version of the gasifier has been developed. This work was initiated in Germany in the 1954 to 55 time period, and since then was continued sporadically in Britain.

The top of the slagging gasifier is identical to the dry ash unit, while the bottom part has been modified. The ash melts at the high temperatures reached in the combustion zone, up to 2,000°C (3,630°F), and forms a slag which runs into the quench chamber – a water bath in which the slag forms small granules of solid ash. Temperatures, and therefore reaction rates, are high in the gasification zone so that the coal residence time is approximately 20 minutes, or one-third of that in the dry ash Lurgi. Steam decomposition approaches 100%, and because the off gas now has less heat capacity, top temperatures are very much dependent on the moisture content of the coal, as is the steam content of the off gas.

In addition to improved steam decomposition, the higher temperatures also result in lower carbon dioxide concentrations due to the formation of carbon monoxide via the Boudouard reaction. The hydrogen-to-carbon monoxide ratio in the off gas is typically 0.5 in comparison with 2 for the dry ash Lurgi. The off gas still contains methane, but this is probably derived from devolatilization at the top of the gasifier rather than by carbon hydrogenation. The off gases in fact contain more tars and oils than in the dry ash system, apparently because of the lower heat capacity of the off gases and consequently lower top temperatures.

See also: Gasification, Gasifiers.

Sludge

Sludge is a type of chemical waste is waste is a general term and covers many types of materials but is generally recognized as a waste that is composed of harmful chemicals. Thus, by this definition, organic chemical waste is composed of harmful chemicals. On the other hand, activated sludge consists of sludge particles containing living organisms, produced in either raw or settled wastewater by the growth of organisms (which include bacteria) in aeration tanks where dissolved oxygen is present.

The wastewater treatment industry describes sludge as a waste stream resulting from wastewater treatment. This description does not provide a physical or chemical basis for a definition but is adequate for the needs of wastewater treatment plant (WWTP) operations (i.e., anyone can distinguish between the treated effluent, which flows out of the plant, and the material that is pumped, scraped, or skimmed from the treatment units).

One option is to define sludge on the basis of the solids content (Figure S-1), but in order to develop a quantitative definition of sludge which will also help with correlating waste forms with disposal options, a simple and measurable characteristic of all three waste forms needs to be identified.

<i>Waste form</i>	<i>Solid,</i>	<i>Sludge</i>	<i>Liquid</i>
<i>Total solids, % w/w</i>	50 to 100	1 to 50	<1%

Figure S-1 Simplified distinction between solid waste, sludge, and liquid waste.

See also: Activated Sludge Process, Chemical Waste.

Slurry Phase Reactor

The latest development of Fischer-Tropsch technology is the Sasol slurry phase reactor, which might also be applicable to the production of fuels from biomass. This reactor is an integral part of the Sasol slurry phase distillate

(SSPD) process, and carries out the synthesis gas reaction at low temperatures (200 to 250°C; 390 to 480°F) and low pressures.

The process involves bubbling hot synthesis gas through a liquid slurry of catalyst particles and liquid reaction products. Heat is removed from the reactor via coils within the bed producing steam. Liquid products are removed from the reactor, and the liquid hydrocarbon wax separated from the catalyst. The gas stream from the top of the reactor is cooled to recover low-boiling hydrocarbon derivatives and reaction water. The Sasol slurry phase technology has undergone several developments primarily concerned with catalyst formulations. Initial development used an iron-based catalyst, but recent developments have used a cobalt-based catalyst, giving greater conversion.

See also: Synthesis Gas.

Smog

Smog (a term that is a combination of the words smoke and fog) is made up of suspended particulates, which are formed by a complex reaction between various oxides of nitrogen and a wide range of hydrocarbon derivatives, which is triggered by sunlight. Smog is a combination of various gases with water vapor and dust. A large part of the gases that form smog is produced when fuels are burnt. Smog forms when heat and sunlight react with these gases and fine particles in the air. Smog can affect outlying suburbs and rural areas as well as big cities. Its occurrences are often linked to heavy traffic, high temperatures, and calm winds. Heavy smog greatly decreases ultraviolet radiation. Smog and acid rain might be considered to be the end-point of emissions from the use of natural gas.

Particulate emissions also cause the degradation of air quality in the United States. These particulates can include soot, ash, metals, and other airborne particles. In fact, sulfur and nitrate effluents form small particles $PM_{2.5}$ (particulate matter that is on the order of 2.5 microns in diameter) that can (and will) irritate eyes and nasal cavity, also particulate matter ($PM_{2.5}$) can enter the blood stream of humans (and animals) and adversely affect the heart and lungs.

Global warming or the greenhouse effect is an environmental issue that deals with the potential for global climate change due to increased levels of atmospheric greenhouse gases. There are certain gases in the atmosphere that serve to regulate the amount of heat that is kept close to the surface of the Earth. Scientists theorize that an increase in these greenhouse gases will translate into increased temperatures around the globe, which would result in many disastrous environmental effects.

The principle greenhouse gases include water vapor, carbon dioxide, methane, nitrogen oxides, and some engineered chemicals such as chlorofluorocarbons. While most of these gases occur in the atmosphere naturally, levels have been increasing due to the widespread burning of fossil fuels by growing human populations. The reduction of greenhouse gas emissions has become a primary focus of environmental programs in countries around the world.

One of the principle greenhouse gases is carbon dioxide. Although carbon dioxide does not trap heat as effectively as other greenhouse gases (making it a less potent greenhouse gas), the sheer volume of carbon dioxide emissions into the atmosphere is high, particularly from the burning of fossil fuels.

Because carbon dioxide makes up such a high proportion of U.S. greenhouse gas emissions, reducing carbon dioxide emissions can play a huge role in combating the greenhouse effect and global warming. The combustion of natural gas emits almost 30% less carbon dioxide than oil, and just under 45% less carbon dioxide than coal.

One issue that has arisen with respect to natural gas and the greenhouse effect is the fact that methane, the principle component of natural gas, is itself a very potent greenhouse gas. In fact, methane has an ability to trap heat almost 21 times more effectively than carbon dioxide.

Methane emissions account for only 1.1% of total U.S. greenhouse gas emissions, they account for 8.5% of the greenhouse gas emissions based on global warming potential. Sources of methane emissions in the U.S. include the waste management and operations industry, the agricultural industry, as well as leaks and emissions from the oil and gas industry itself. A major study performed by the Environmental Protection Agency (EPA) and the Gas Research Institute (GRI) in 1997 sought to discover whether the reduction in carbon dioxide emissions from increased natural gas use would be offset by a possible increased level of methane emissions. The study concluded that the reduction in emissions from increased natural gas use strongly outweighs the detrimental effects of increased methane emissions. Thus, the increased use of natural gas in the place of other, dirtier fossil fuels can serve to lessen the emission of greenhouse gases in the United States.

Smog and poor air quality are a pressing environmental problem, particularly for large metropolitan cities. Smog, the primary constituent of which is ground level ozone, is formed by a chemical reaction of carbon monoxide, nitrogen oxides, volatile organic compounds, and heat from sunlight. As well as creating that familiar smoggy haze commonly found surrounding large cities, particularly in the summer time, smog, and ground-level ozone can contribute to respiratory problems ranging from temporary discomfort to long-lasting, permanent lung damage. Pollutants contributing to smog come from a variety of sources, including vehicle emissions, smokestack emissions, paints, and solvents. Because the reaction to create smog requires heat, smog problems are the worst in the summertime.

The use of natural gas does not contribute significantly to smog formation, as it emits low levels of nitrogen oxides, and virtually no particulate matter. For this reason, it can be used to help combat smog formation in those areas where ground-level air quality is poor. The main sources of nitrogen oxides are electric utilities, motor vehicles, and industrial plants. Increased natural gas use in the electric generation sector, a shift to cleaner natural gas vehicles, or increased industrial natural gas use could all serve to combat smog production, especially in urban centers where it is needed the most. Particularly in the summertime, when natural gas demand is lowest and smog problems are the greatest, industrial plants and electric generators could use natural gas to fuel their operations instead of other, more polluting fossil fuels. This would effectively reduce the emissions of smog causing chemicals, and result in clearer, healthier air around urban centers. For instance, a 1995 study by the Coalition for Gas-Based Environmental Solutions found that in the Northeast, smog and ozone-causing emissions could be reduced by 50 to 70% through the seasonal switching to natural gas by electric generators and industrial installations.

Particulate emissions also cause the degradation of air quality in the United States. These particulates can include soot, ash, metals, and other airborne particles. Natural gas emits virtually no particulates into the atmosphere: in fact, emissions of particulates from natural gas combustion are 90% lower than from the combustion of oil, and 99% lower than burning coal.

Acid rain is another environmental problem that affects much of the Eastern United States, damaging crops, forests, wildlife populations, and causing respiratory and other illnesses in humans. Acid rain is formed when sulfur dioxide and nitrogen oxides react with water vapor and other chemicals in the presence of sunlight to form various acidic compounds in the air. The principle source of acid rain-causing pollutants, sulfur dioxide and nitrogen oxides, are coal-fired power plants. Since natural gas emits virtually no sulfur dioxide, and up to 80% less nitrogen oxides than the combustion of coal, increased use of natural gas could provide for fewer acid rain-causing emissions.

See also: Acid Rain, Greenhouse Effect.

Smog Formation

Smog is a pressing environmental problem, particularly for large metropolitan cities. The primary constituent of smog is ground-level ozone created by photochemical reactions in the near-surface atmosphere involving a combination of pollutants from many sources, including motor vehicle exhausts, volatile organic compounds such as paints and solvents, and smokestack emissions. Because the reaction to create smog requires heat, smog problems are the worst in the summertime.

Natural gas use is not much of a factor in smog formation. As opposed to crude oil products and coal, the combustion of natural gas results in relatively small production of smog-forming pollutants as it emits low levels of nitrogen oxides, and virtually no particulate matter. For this reason, it can be used to help combat smog formation in those areas where ground-level air quality is poor. The smog-forming pollutants literally cook in the air as they mix together and are acted on by heat and sunlight. The wind can blow smog-forming pollutants away from their sources while the reaction takes place, explaining why smog can be more severe miles away from the source of pollutants than at the source itself.

See also: Acid Rain, Atmosphere.

Sodasol Process

During washing with lye solution (alkaline solution), the lye removes only the lighter or lower-boiling mercaptans, but various chemicals can be added to the lye solution to increase its ability to dissolve the higher-boiling mercaptan

derivatives. The added chemicals are generally known as solubility promoters or solutizers that differ chiefly in the composition of the solutizers.

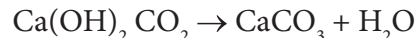
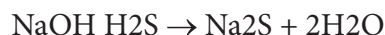
In the process, the treating solution is composed of lye solution and alkyl phenols (acid oils), which occur in cracked naphtha and cracked gas oil and are obtained by washing cracked naphtha or cracked gas oil with the lye solution. The lye solution, with solutizers incorporated, is then ready to treat product streams, such as straight-run naphtha and kerosene. The process is carried out by pumping a sour stream up a treating tower countercurrent to a stream of Sodalol solution that flows down the tower. As the two streams mix and pass, the solution removes mercaptans and other impurities, such as oxygen compounds (phenols and acids), as well as some nitrogen compounds.

The treated stream leaves the top of the tower; the spent Sodalol solution leaves the bottom of the tower to be pumped to the top of a regeneration tower, where mercaptans are removed from the solution by steam. The regenerated Sodalol solution is then pumped to the top of the treatment tower to treat more material.

A variation of the Sodalol process is the Potasol process, which uses potassium hydroxide instead of lye (sodium hydroxide).

Sofnolime RG Process

The Sofnolime RG process is an *alkaline solids dry sorption process* that makes use of a hydroxide media similar to that of caustic scrubbing processes. It is a dry process that claims it has a synergistic mixture of hydroxides in a granular solid. The media is capable of removing H₂S, CO₂, COS, SO₂, and organic sulfur compounds. The process employs the following reactions:



Sofnolime RG removes both H₂S and CO₂. Gas streams with high carbon dioxide content will exhaust the media rapidly. The packed bed is supported between layers of ceramic balls on the top and bottom, with the flow direction in the upward direction.

Softwood

In the current context of using wood as an alternate energy source, a description of the different types of pore system is worthy of note since the type of wood and the distribution patterns of the pore systems can have a strong influence the processibility of the wood.

As with hardwood, becoming familiar with wood characteristics and structure, as well as the techniques used to identify them, requires practice and dedication. If you know what to look for and where to look to identify any unique characteristics, thereby enabling accurate and efficient wood identification.

The first step after making the determination that a wood specimen is softwood – due to the absence of pores – is to inspect the cross-section surface for the presence of resin canals. Resin canals are tubular passages in wood that exude pitch, or resin, to seal off wounds that occur due to insect or mechanical damage. Resin canals most often occur in or near the latewood zone of the growth rings. Softwoods can be separated into two classifications based on the presence or absence of resin canals. Species that have resin canals include pine trees, spruce trees, larches, and Douglas fir trees. The species that do not have resin canals include firs, hemlocks, cedars, redwood, bald cypress, and yew.

Woods with resin canals are further separated into two groups: (i) those with large resin canals, such as pines, and (ii) those with small resin canals, such as Douglas fir, spruce, and larch. Using a sample wood identification set to compare the size and number of resin canals of different species is useful in determining how much they

can differ between species. For example, most pines have quite large and numerous resin canals that can be seen without the aid of a hand lens. Spruce and larch, on the other hand, have much smaller resin canals that occur less frequently. Douglas fir has many small resin canals. Because the presence of resin canals is quite variable, it may be necessary to make several cuts on the cross section of a specimen to uncover enough surface area to make a good determination.

As with the hardwoods, color, odor, and density are useful characteristics in identifying softwoods. Some species have distinct color differences, while others do not. Eastern white pine is consistently yellowish white, darkening to light brown with age. Eastern redcedar has a distinctive deep purplish-red color, and redwood a deep reddish-brown. Examples of odors include the pine-type fragrance of pines, the cedar-type scent of eastern red cedar, and the relative absence of smell in spruce trees and fir trees.

Softwoods also vary substantially in density. Because many species are quite dense and strong, softwood lumber is typically used for structural or construction purposes. Southern yellow pine, spruce, hemlock, fir, and Douglas fir are all commonly used in the construction industry. White pine and cedars, on the other hand, are considerably less dense and lighter in weight than the other species, while white pine and cedars are easier to slice with a razor blade when preparing a surface for identification.

See also: Hardwood, Wood, Wood – Hardwood, Wood – Softwood.

Softwood Residues

Softwood residues are generally in high demand as feedstocks for paper production, but hardwood timber residues have less demand and fewer competing uses. In the past, as much as 50% of the tree was left on site at the time of harvest. Whole tree harvest systems for pulp chips recover a much larger fraction of the wood. Wood harvests for timber production often generates residues which may be left on the site or recovered for pulp production. Economics of wood recovery depend greatly on accessibility and local demand. Underutilized wood species include Southern red oak, poplar, and various small diameter hardwood species.

Unharvested dead and diseased trees can comprise a major resource in some regions. When such timber has accumulated in abundance, it comprises a fire hazard and must be removed. Such low-grade wood generally has little value and is often removed by prescribed burns in order to reduce the risk of wildfires.

See also: Biomass, Wood, Wood Biomass.

Soil

Soil is an important aspect of any environmental studies because, on the land, the soil is often the major recipient of any spilled chemical(s). Soil covers most of the land surfaces as a continuum, and each soil grades into the rock materials below and into other soils at its margins, where changes occur in relief, groundwater, vegetation, kinds of rock, or other factors which influence the development of soils. The organic and inorganic material in which soils form is the parent material. Soil can be conveniently subdivided into various soil types, each with different composition and properties (Table S-1, Table S-2).

Table S-1 Types of soils based on composition.

Classification	% w/w clay	% w/w silt	%w/w sand
Clay soil	40-100	0-40	0-45
Loam soil	7-27	28-50	23-52
Sandy soil	1-10	1-15	85-100%

Table S-2 Types of soils based on properties.

Soil type*	Descriptions
Alluvial soil	Formed as a result of deposition by the rivers and streams; lacks a well-developed profile; supports luxuriant growth of vegetation.
Chernozemic soil	Occurs in humid to semi-arid temperate climatic conditions under grasses.
Desertic soil	Found in arid climatic conditions.
Latosolic soil	Develops in humid tropical or semitropical-forested regions.
Mountain soil	Occurs in hilly regions under colder climates.
Podzolic soil	Also called podzolonc soil; found in humid temperate climate, under forest vegetation.
Saline soil	Occurs in the dry climates where rapid evaporation of water results in surface deposition.
Tundra soil	Develops in colder regions and under vegetation such as lichens, mosses, herbs, and shrubs.

*Listed alphabetically.

The formation of soil involves the formation of unconsolidated materials by the weathering which leads to the development of the soil profile. During weathering, the physical disintegration and chemical decomposition of the rocks and minerals contained in them occurs. The physical disintegration process is the breakdown of rock into smaller fragments and eventually into sand and silt particles that are commonly made up of individual minerals. Simultaneously, mineral decomposition occurs and soluble materials released and new minerals are often created. The new minerals form either by minor chemical alterations or by a complete chemical breakdown of the original mineral, thereby leading to the creation of new minerals. Based on the location of soil mineral particles formation and deposition, the soils are classified as *residual soil* and *transported soil*. Residual soil is the soil that has been formed in place from the bedrock below. On the other hand, transported soil is soil in which the mineral particles have been carried from some other location by wind, water, gravity, or ice. Furthermore, the transported soil can be classified (alphabetically) into (i) alluvium, which is soil that has been transported by the movement of water, (ii) colluvium, which is soil that has been transported by gravity, (iii) eolian soil, which is soil that has been transported by wind, and (iv) glacial soil, which is soil that has been transported by the movement of glaciers.

Mineral soils that are formed directly from the weathering of bedrock, the solid rock that lies beneath the soil; therefore, they have a similar composition to the original rock. Other soils form in materials that came from elsewhere, such as sand and glacial drift. Materials located in the depth of the soil are relatively unchanged compared with the deposited material. Sediments in rivers may have different characteristics, depending on whether the stream moves quickly or slowly. A fast-moving river could have sediments of rocks and sand, whereas a slow-moving river could have fine-textured material, such as clay.

Thus, soil is a mixture of organic matter, minerals, gases, and liquids, and organisms that together support life on the Earth. The soil on the earth (the pedosphere) has four important functions which are (i) a medium for plant growth, (ii) a medium for water storage, supply, and purification, (iii) a modifier of the atmosphere of the Earth, and (iv) a habitat for organisms. The soil is the most important part of any land system insofar as it is the medium upon which virtually all terrestrial organisms depend upon it for their existence. The productivity of soil is strongly affected by environmental conditions and pollutants.

Soil is a product of several factors, some of which are (i) the influence of climate, (ii) elevation, orientation, and slope of terrain, (iii) organisms, and (iv) the parent materials of the soil (i.e., the original minerals) interacting over time. Also, the soil continually undergoes development by way of numerous physical, chemical, and biological processes, which include weathering and the associated erosion.

Most soils have a dry bulk density (density of soil taking into account voids when dry) between 1.1 g/cm^3 and 1.6 g/cm^3 , while the soil particle density is much higher, typically in the range of 2.6 to 2.7 g/cm^3 . In engineering terms, soil is included in the broader concept of regolith, which also includes other loose material that lies above the bedrock, as can be found on the Moon and on other celestial objects as well.

Soil is the receptor of chemical waste from landfill leachate, lagoons, and other sources. Contamination of the soil refers to addition of soil constituents, due to domestic, industrial, and agricultural activities, that were originally absent in the system. Soil contamination is of two different kinds: (i) the slow but steady degradation of soil quality (such as organic matter, nutrients, water-holding, capacity, porosity, and purity) due to contaminants such as domestic and industrial wastes or chemical inputs from agriculture, and (ii) the concentrated pollution of smaller areas, mainly through dumping or leakage of wastes. The sources of contamination include the weathering of geological parent materials, where element concentrations exceed the natural abundances in wet or dry deposition forms. More specifically, a number of metals and chemicals are commonly regarded as contaminants of soil and include heavy metals as well as metalloids and nonmetals. The main elements implicated as contaminants are arsenic, cadmium, chromium, copper, fluorine, lead, mercury, nickel, and zinc. In addition, beryllium, bismuth, selenium, and vanadium may also be dangerous.

In some cases, land farming of degradable organic wastes is practiced as a means of disposal and degradation. The degradable material is worked into the soil, and soil microbial processes cause the degradation of the material, as for example by the application of sewage and fertilizer-rich sewage sludge to soil.

Soil is a finely divided rock-derived material containing organic matter and capable of supporting vegetation. Soils are independent natural bodies, each with a unique morphology resulting from a particular combination of climate, living plants and animals, parent rock materials, relief, the groundwater, and age.

Soil is a variable mixture of minerals, organic matter, as well as water and is the final product of the weathering action of physical, chemical, and biological processes on rocks. The organic portion of soil consists of plant biomass in various stages of decay. High populations of bacteria, fungi, and animals such as earthworms may be found in soil. The presence of living organisms greatly affects soil formation and structure. Animals and microorganisms can produce pores and crevices. Plant roots can penetrate into crevices to produce more fragmentation. Plant secretions promote the development of microorganisms around the root in an area known as the rhizosphere. Additionally, leaves and other material that fall from plants decompose and contribute to soil composition.

Approximately 35% v/v of a typical soil is composed of air-filled pores. As a point of reference, the atmosphere at sea level contains 21% v/v oxygen and <0.1% v/v carbon dioxide. These amounts may be quite different in soil air because of the decay of organic matter which produces carbon dioxide by consumption of oxygen. As a result, the oxygen content of air in soil may be as low as 15% v/v and the carbon dioxide content may be several percent.

The description of the soil profile commences at the underlying rock which supplies the parent material for the formation of soil; a series of layers are developed. Each layer is called a soil horizon and the sequence of horizons. There are five main types of horizons (layers) in soil which are denoted as O, A, B, C, and R horizons. Each horizon is different from the others in terms of the properties, such as color, texture, structure, consistency, porosity, and reactivity.

The O-horizon is the topmost portion of soil and consists of organic matter and is commonly found in forest soils. It is further subdivided into (i) the O1 horizon, which is the organic horizon wherein the original forms of plant and animals residues can be recognized by the naked eye, the O2 horizon in which the original plant and animal forms cannot be distinguished by the naked eye, (ii) the A-horizon is the mineral horizon, which lies at or near the surface and is recognized as the zone of maximum leaching or eluviation, and (iii) the B-horizon which is the layer below the A layers in which there is the accumulation of iron and aluminum oxide and silicate clay minerals the occurs and is sometimes also referred to as subsoil and is further divisible in B1, B2, and B3 horizons. The R Horizon represents the bedrock from which the other horizons may have originated (Sigel and Sigel, 1995).

Typically, the A, B, C, and R horizons are parallel (or near-parallel) to the surface of the Earth and may be thick or thin. The horizons may be prominent or so weak that they can be detected only in the laboratory. In general, the boundary of soils with the underlying rock or rock material occurs at depths ranging from 1 to 6 feet, though the extremes lie outside this range. Rainwater percolating through soil carries dissolved and colloidal solids to lower horizons where they are deposited.

One of the more important classes of productive soils is the podzol type of soil which are soils formed in temperate-to-cold climates under relatively high rainfall conditions under coniferous or mixed forest or heath vegetation. These generally rich soils tend to be acidic (pH 3.5-4.5) such that alkali and alkaline earth metals and, to a lesser extent aluminum and iron, are leached from the A horizon, leaving kaolinite as the predominant clay mineral. At somewhat higher pH in the B horizon, hydrated iron oxides and clays are redeposited.

The mechanical properties of soil are largely determined by particle size. The four major categories of soil particle sizes are (i) gravel, 2 to 60 mm, (ii) sand, 0.06 to 2 mm, (iii) silt, 0.06 to 0.006 mm, and (iv) clay minerals, <0.002 mm. Clays represent a size fraction rather than a specific class of mineral matter. Soil receives large quantities of contaminants as a result of a variety of activities. Pesticides are a particular contaminant because of their application to crops.

Cation exchange in soil is the mechanism by which potassium, calcium, magnesium, and essential trace-level metals are made available to plants. When nutrient metal ions are taken up by plant roots, a hydrogen ion is exchanged for the metal ions. This process, and the leaching of calcium, magnesium, and other metal ions from the soil by water containing carbonic acid, tends to make the soil acidic.

In addition to being the site of most food production, soil is the receptor of large quantities of pollutants, such as particulate matter from power plant smokestacks. Fertilizers and some other materials applied to soil often contribute to water and air pollution. Therefore, soil is a key component of environmental chemical cycles; soils are open systems that undergo continual exchange of matter and energy with the atmosphere, hydrosphere, and biosphere.

Solar Collectors

Typically, the term solar collector refers to a device that collects and/or concentrates solar radiation from the Sun. These devices are primarily used for active solar heating and allow for the heating of water for personal use. These collectors are generally mounted on the roof and must be very sturdy as they are exposed to a variety of different weather conditions. As well as in domestic settings, a large number of these collectors can be combined in an array and used to generate electricity in solar thermal power plants.

There are many different types of solar collectors (examples are presented below), but all are constructed with the same basic premise in mind. In general, there is some material that is used to collect and focus energy from the Sun and use it to heat water. The simplest of these devices uses a black material surrounding pipes that water flows through. The black material absorbs the solar radiation very well, and as the material heats up the water it surrounds. This is a simple design, but collectors can be complex. Absorber plates can be used if a high temperature increase isn't necessary, but generally, devices that use reflective materials to focus sunlight result in a greater temperature increase.

Evacuated Tube Collectors

This type of collector features rows of glass tubes placed parallel to each other with a vacuum between them that insulates the tubes and helps hold on to the heat. The tubes are also transparent and covered with a coating. Inside each tube is an absorber with liquid inside it. When light from the sun hits the tube and its radiation is absorbed by the absorber, the liquid inside is heated. Because of the vacuum between the tubes, this liquid can be heated to high temperatures, up to 175°C (350°F). Though the evacuated tube collectors can achieve high temperatures, they are more fragile than other types of solar collectors and more expensive.

Flat Plate Collectors

The most common type of energy collector, the flat plate collector, is a rectangular-shaped box that is put on the roof of the home or building where the solar water heating system is located. Inside the box is a thin absorber sheet, usually black in color and made of either copper or aluminum. Behind the sheet is a tubing system in the form of a grid or coils. The collector and tubing system are put inside an insulated casing. The cover is usually glass and transparent. This glass is often black or a dark color that draws in the sunlight.

As the sun shines, the heat builds up in the collector and heats the fluid that is inside the tubes. If it is water, it is heated and passes through a storage tank. If the fluid inside is antifreeze, the water is heated by circulating the heated solution through a tube inside the storage tank in which the water is located.

Line Focus Collectors

Line focus collectors (sometimes known as parabolic troughs) use highly reflective materials to collect and concentrate the heat energy from solar radiation. These collectors are composed of parabolically shaped reflective sections connected into a long trough. A pipe that carries water is placed in the center of this trough so that sunlight collected by the reflective material is focused onto the pipe, heating the contents. These are high-powered collectors and are

thus generally used to generate steam for solar thermal power plants and are not used in residential applications. These troughs can be extremely effective in generating heat from the Sun, particularly those that can pivot, tracking the Sun in the sky to ensure maximum sunlight collection.

Point Focus Collectors

Point focus collectors are large parabolic dishes composed of some reflective material that focus the Sun's energy onto a single point. Although effective at collecting sunlight, the point focus collectors must actively track the Sun across the sky to be of any value. These dishes can work alone or be combined into an array to gather even more energy from the Sun.

Point focus collectors and similar apparatuses can also be utilized to concentrate solar energy for use with concentrated photovoltaics. In this case, instead of producing heat, the energy of the Sun is converted directly into electricity with high efficiency photovoltaic cells designed specifically to harness concentrated solar energy.

Solar Energy

Solar energy is energy from the Sun, and in terms of alternative energy, *solar energy* refers to the energy that is harnessed from solar radiation, using the radiant light and heat from the Sun for practical purposes. The term solar power either is used synonymously with solar energy or is used more specifically to refer to the conversion of sunlight into electricity. Solar energy can be harnessed at different levels around the world, mostly depending on distance from the equator.

The Sun is most prominent source of energy in the solar system. The source of solar energy is the process of thermonuclear fusion in the core of the Sun. This energy is radiated from sun in all directions, and a fraction of this energy reaches to the earth. The outer visible layer of the Sun (the photosphere) has a temperature on the order of 6,000°C (10,800°F). Above the photosphere, there is a transparent layer of gases known as chromospheres. The light emitted by the chromospheres is of short wave length. Finally, there is the corona. The corona is the outer part of the atmosphere of the Sun – in this region, the prominence appears. Prominence is immense clouds of glowing gas that erupt from upper chromospheres. The corona can only be seen during total solar eclipse.

The Earth receives the solar energy in the form of solar radiation. These radiations are comprised of ultraviolet, visible, and infrared radiation. The amount of solar radiation that reaches any given location is dependent on several factors like geographic location, time of day, season, land scope, and local weather. Because the Earth is round, the Sun rays strike the Earth's surface at different angles ranging from 0 to 90°. When the rays of the Sun are vertical, the Earth receives the maximum possible energy.

Generally, almost all renewable energies, notably excluding geothermal energy and tidal energy, derive the energy from the sun. For example, winds blow partly because of absorption of solar radiation by the atmosphere of the Earth. Solar energy radiant light and heat from the Sun are harnessed using a range of ever-evolving technologies such as solar heating, solar photovoltaics, solar thermal electricity, solar architecture, and artificial photosynthesis.

There are many technologies for harnessing solar energy within these broad classifications: (i) active solar energy, (ii) passive solar energy, (iii) direct solar energy, and (iv) indirect solar energy.

Active solar energy systems use electrical and mechanical components such as tracking mechanisms, pumps, and fans to capture sunlight and process it into usable outputs such as heating, lighting, or electricity. On the other hand, passive solar systems use non-mechanical techniques to control the capture of sunlight and distribute this energy into usable outputs such as heating, lighting, cooling, or ventilation. These techniques include selecting materials with favorable thermal properties to absorb and retain energy, designing spaces that naturally circulate air to transfer energy and referencing the position of a building to the Sun to enhance energy capture. In some cases, passive solar devices can have mechanical movement with the important distinction that this movement is automatic and directly powered by the Sun.

Direct solar energy generally refers to technologies or effects that involve a single-step conversion of sunlight that results in a usable form of energy, while indirect solar energy generally refers to the generation of energy using technologies or effects that involve multiple-step transformations of sunlight that eventually result in a usable form of energy.

Collecting solar radiation and converting it into electricity – the production of solar power – can be achieved in two ways which are (i) directly using photovoltaic devices (PV devices, also referred to as solar cells), or (ii) indirectly using solar thermal/electric power plants. The first method involves grouping individual photovoltaic cells into panels and arraying panels, ranging from small cells to power watches and calculators to those that power single homes to those that produce electricity in power plants covering many acres. The second way uses concentrated solar power (CSP), whereby lenses or mirrors to concentrate a large area of sunlight, or solar thermal energy, onto a small area. Electrical power is produced when the concentrated light is converted to heat, which drives a heat engine (usually a steam turbine) connected to an electrical power generator or powers a thermochemical reaction.

The main benefits of solar energy are: (i) solar energy systems do not produce air pollutants or carbon-dioxide, and (ii) when located on buildings, they have minimal impact on the environment. However, the limitations are (i) the amount of sunlight that arrives at the surface of the Earth is not constant, and it varies depending on location, time of day, time of year, and weather conditions and (ii) the Sun does not deliver a constant amount of energy to any one place at any one time; a large surface area is required to collect the energy at a useful rate. This second limitation can be overcome by the use of storage batteries that preserve the stored energy until required. In fact, solar energy is a renewable resource and there is no limit to its renewability, at least not until the Sun burns itself out billions of years from now. Solar energy also does not contribute to pollution and thus is considered a “clean” energy source. Using it produces no greenhouse gases and thus does not contribute to global climate change.

However, a disadvantage is that solar technology is not available on demand in every location on the Earth. Heavy cloud cover can limit the use of some solar energy systems. Some systems cannot be used at all if direct sunlight is not available. In most areas of the world, only low-power solar energy applications can be used because of the lack of direct sunlight. Also, for large-scale projects such as solar power towers and solar furnaces, or even smaller-scale projects such as solar ponds, dish systems, and trough systems, large areas of land are needed. In the desert, where a number of these systems are currently located, the solar technology that is put there to capture the intense sunshine is considered unsightly by some people.

Also, solar energy can have both positive and negative effects on the environment. On the positive side, most solar technologies are environmentally friendly and (i) do not pollute the atmosphere by emitting greenhouse gases, (ii) do not produce radioactive waste as occurs in nuclear reactors, and (iii) do not contribute to global climate change or acid rain. Most solar energy systems are silent or quiet when they operate, which decreases noise pollution.

The benefits of solar energy systems include the potential in terms of energy hitting the Earth, the low environmental impact, and the lack of producing carbon dioxide and air pollutants. Limitations preventing the large-scale implementation of solar-powered energy generation is the inefficiency of current solar technology and the cost. In addition, the amount of sunlight varies depending on weather conditions, location, time of day, and time of year, and the need for a large surface to collect the energy, since it does not deliver concentrated energy at any one place.

See also: Photovoltaic Cells, Solar Energy – Active, Solar Energy – Passive, Steam Turbine.

Solar Energy – Active

Active solar energy systems include solar collectors (also known as solar panels), which are primarily used on solar hot water heaters; photovoltaic (PV) cells, which make electricity; and concentrated solar power systems (also known as solar thermal systems), which also make electricity but on a larger scale than photovoltaic cells.

Solar collectors are used primarily to capture solar energy for use in solar hot water heaters. However, they can also be used to provide heat in a building and even to make the energy to cool a building. While not all solar collectors are used in active solar energy systems, it is more common for solar collectors to be used in an active system than a passive system.

Photovoltaic cells convert sunlight directly into electricity inside the cell. They are more adaptable than many other types of solar energy technology. In addition to powering satellites, photovoltaic cells can be put on buildings to provide electricity for any number of uses and do not require direct sun to convert sunlight into electricity.

There are at least five types of concentrated solar power systems that focus the Sun's power to make electricity on a larger scale than photovoltaic cells and include (i) solar ponds, (ii) parabolic trough systems, (iii) dish systems and dish-engine systems, (iv) solar power towers, and (v) solar furnaces. Mirrors or other reflective devices draw in as

much sunlight as possible to these systems. They often track the Sun as it moves through the sky in order to capture the most sunlight.

Concentrated solar power systems usually heat water, or another fluid that is connected to a source of water, to make steam. The steam is used to drive turbines that create electricity. Concentrated solar power systems are primarily used for industrial applications and to make electricity for consumers and businesses on a wide scale.

See also: Solar Energy, Solar Energy – Passive, Steam Turbine.

Solar Energy – Passive

Passive solar systems are primarily concerned with the design of buildings, homes, and lighting. Passive solar design focuses on the placement of the home or building and on windows, ventilation, and insulation to cut down on the need for electricity by using the Sun. The home or building is designed to maximize the potential of solar energy for heating and cooling. In northern countries where sunshine is not as strong as it is in locations to the south, passive solar heating is one of the easiest forms of solar technology to use.

One important form of passive solar design is known as daylighting which involves the placement and design of windows used to encourage natural sunlight to light the inside of a building instead of electric lights. Daylighting helps cut down on lighting costs, and many experts believe that exposure to natural rather than artificial light sources provides health benefits to humans. Another type of passive solar system is the transpired solar collector. This is a relatively new passive solar technology made of dark perforated metal. Transpired solar collectors are used to heat buildings by heating the air. They can also cool buildings in summertime.

There are five basic types of passive solar design systems: (i) the direct gain type, (ii) thermal storage, (iii) solar greenhouse, (iv) roof pond, and the convective loop.

The direct gain technology is the simplest type of passive solar design. In this system, a large number of windows in a building are set up to face south (in the Northern Hemisphere). The glass is usually double-paned or even triple-paned. That is, the glass consists of two to three panes of glass with a pocket of air in between each pane. Each pane is sealed inside one frame. Materials that can absorb and store the Sun's heat can be incorporated into the floors and walls that are hit by the Sun. These floors and walls release the heat at night when it is needed the most to heat the building.

The thermal storage technology is similar to the direct gain technology. In this system, there is also a large wall oriented to the south in the Northern Hemisphere. This wall is placed behind double-glazed windows so that it can absorb sunlight. In some of these thermal storage systems, the wall contains a storage medium such as masonry or perhaps water. The solar energy that is collected is stored during daylight hours so that it can be released when there is no Sun.

The solar greenhouse technology is also known as the sunspace technology which is a combination of both direct gain and thermal storage but are located in a greenhouse. The wall of the thermal storage system is placed next to the greenhouse and the home to which it is attached. This system primarily heats the greenhouse but also can provide heat to the house itself.

As the name implies, the roof pond technology consists of ponds of water placed on a roof which are exposed to the Sun, collect the radiation from the Sun, and store it. The heat that is produced is controlled by insulating panels that are movable. During the winter, these panels are open during daylight hours so that sunlight can be collected. During nighttime hours, the panels are closed so that little or no heat is lost. The heat that is collected is released into the building to warm it. During the summer, roof ponds are used in the opposite way. The panels are closed during the day to block the heat of the sun. At night, they are opened to allow cooling of the building.

The convective loop technology is also known as a natural convective loop technology in which a collector is located below the building's living space. The hot air that is created from solar energy rises to heat this living space when needed.

Daylighting, also known as passive lighting, is a form of passive solar design and involves the use of sunlight to light up the inside of a building. Daylighting can fully replace electric lights, or it can be used to cut down on electrical costs by supplementing electrical lighting already being used and can also be used to heat a building.

Daylighting primarily occurs through a building's windows, though other kinds of openings on buildings, such as skylights, can also be used. The windows are often large and, in the Northern Hemisphere, face south. Buildings and homes that use daylighting have specific placement and spacing of windows. For example, windows that are higher up on a wall distribute sunlight better. Windows called clerestory windows (a row of windows located at the top of a wall, near the roof) are an important part of daylighting in museums and churches. Skylights, when combined with sensors and other lighting elements, can ensure that lighting inside a building stays even.

Windows used in daylighting absorb sunlight and release it slowly to light up a building. One way to regulate the amount of sunlight and/or heat is through window shades or curtains that are insulating. Light shelves can also be used. They are placed so that the sunlight drawn in by the windows is reflected and lights a room from top to bottom. These shelves can bring natural light deeper into a room.

Chemical compounds in windows for daylighting can be made part of window glass or placed between the panes of double- and triple-paned windows. These compounds can boost how much solar energy a window can store. They can also increase the insulating capacity of windows. In addition, coatings and glazing on the windows can control the amount of light or heat. The heating effect of daylighting can be increased by window coatings that are antireflective. Some window coatings can carry an electric current that can moderate how much light or heat is let in based on current weather conditions. One type of glazing can allow a measured amount of light to pass through a window while keeping heat out.

In daylighting systems where natural light is used with electrical lighting, there is the need for a control system. This control system regulates the amount of electric light used based on how much daylighting is available. The types of controls include photocell sensors, infrared receivers, occupant sensors, dimming control systems, and wall-station controls. Building materials and interior design can enhance the effectiveness of daylighting. Walls that are white or brightly colored reflect the light that is drawn inside. In office buildings, cubicle walls kept under a certain height will allow the sunlight to spread over the office.

As daylighting provides light during the day, the amount of heat gain from electric lighting is reduced significantly. Daylighting also makes homes and buildings less gloomy. However, homes and buildings that use daylighting often have to deal with issues such as heat and glare. If the natural lighting is not regulated, the system is not well-designed, or the correct type of window for the local environment is not used, homes and buildings can become hotter than they would were daylighting not used. Daylighting can potentially increase cooling costs during the summer because there is more natural light inside. Daylighting will not work everywhere because there is not enough sunshine in some locations.

Daylighting is difficult to incorporate into buildings that have already been constructed. Even if daylighting is built into a new building, the controls needed to regulate the natural light and electric lights are expensive and require a significant investment. After the system is installed, it must be operated and maintained. People must be trained to deal with the sensors and computer systems that come with many daylighting systems.

See also: Solar Energy, Solar Energy – Active.

Solar Furnace

A solar furnace, in the same manner as a solar power tower, uses mirrors to concentrate sunlight onto one point to achieve high temperatures. The solar energy is collected from over a wide area. Solar furnaces can create higher temperatures than solar towers. There are several types of solar furnaces, each of which produces a different wattage of power.

The best known solar furnace is called a high-flux solar furnace which uses just one flat mirror or heliostat that is large in size and tracks the Sun to ensure the greatest reflection of sunlight onto the primary concentrator. The concentrator consists of twenty-five or so individual curved mirrors. These mirrors focus the light, called a solar flux, at a target inside the building.

The light from the concentrator is focused on a circle or target inside the furnace. The focused beam of light created by the concentrator is much, much stronger than normal sunlight. At its focal point, it can produce the energy of 2,500 suns. There can also be a reflective secondary concentrator added to the focus. The equivalent of up 20,000 suns can then be produced. When a refractive concentrator is added to the system to focus even more light on the

beam, the intensity can equal an amazing 50,000 suns. Temperatures rise very rapidly in a solar furnace, more than 1,000°C (1,830°F) per second. The power level inside the furnace is adjustable by a device called an attenuator, which works like pulling down blinds over a window.

A solar furnace is primarily used to generate heat or steam to make electricity and for industrial use. Steam created by a solar furnace can be used to run generators and industrial equipment. An advantage of using solar-created heat in such industrial processes is that the heat is clean, meaning that it produces no harmful emissions.

See also: Solar Power, Solar Pond, Solar Tower.

Solar Furnace – The Sun

Hydrogen and helium are by far the most common elements in the universe and together account for approximately 98% of all known matter. There is no significant amount of hydrogen or helium in the gaseous state on the Earth because the gravity of small planets is too weak to keep these light atoms attached; they simply escape into outer space. All of the Earth's hydrogen is combined with oxygen as water, with carbon as hydrocarbons, or with other elements in the rocks.

However, the Sun, whose gravity is much stronger, consists almost entirely of hydrogen. The presence of hydrogen in the Sun and the stars can be measured directly from spectroscopic observations since every atom emits light with characteristic *wavelengths* (or colors) that uniquely identify it.

Although there is plenty of hydrogen in the Sun for nuclear fusion, the conditions are such the fusion occurs. The temperature and density of the Sun can be determined by a combination of experimental observations using spectroscopy and by theoretical calculations. The most likely fusion reactions can be deduced from studies of nuclear reactions in the laboratory, using particle accelerators. The energy release in the Sun involves the conversion of four protons into a helium nucleus. However, this does not happen in a single step. First, two protons combine to form a nucleus of the heavy isotope of hydrogen (deuterium, hydrogen-2 or D_2). The deuterium nucleus then combines with another proton to form the light helium isotope (helium-3). Finally two helium-3 nuclei combine to form helium-4, releasing two protons in the process. Overall, four protons are converted into one helium nucleus (Figure S-2) and. As a result, energy is released because the helium nucleus has slightly less mass than the original four protons from which it was formed.

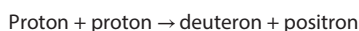


Figure S-2 The reactions that convert hydrogen to helium in the sun.

The total amount of energy released for each conversion of four hydrogen nuclei into a helium nucleus is approximately 10 million times more than is produced by the chemical reaction when hydrogen combines with oxygen and burns to form water. This enormous difference between the energy released by nuclear reactions compared to chemical reactions explains why fusion can sustain the Sun for billions of years.

The energy has to be transported from the Sun's interior core to the surface. This is quite a slow process, and it takes approximately one million years for the energy to get out. The surface of the Sun is cooler than the core, and the energy is radiated into space as the heat and light that can be observed directly. Under standard conditions, the solar power falling on the Earth is approximately 1.4 kilowatts per square meter (1.4 kW m^{-2}). The first stage of the reactions just described is a weak interaction. The process is slow, and this sets the pace for the conversion to helium. It takes many hundreds of millions of years for two protons to fuse together. This turns out to be rather fortunate. If the fusion reaction took place too quickly, then the Sun would have burned out long before life on Earth had a chance to evolve. From the knowledge of the nuclear reaction rates and of the amount of initial hydrogen, it is estimated that the time to use up all the hydrogen is approximately 10 billion years. From the radioactive dating of meteorites, it is estimated that the age of the solar system is 4.6 billion years. Assuming the Sun is the same age as the meteorites, then it is approximately halfway through its life cycle. For comparison, the most recent estimate of the age of the universe is approximately 13.7 billion years.

The proton-proton reaction tends to dominate in stars that are the size of the Sun or smaller. However, in larger stars, there is another reaction cycle, involving reactions with a carbon nucleus, by which protons can be converted into helium nuclei.

Solar Pond

A solar pond is a large, controlled body of water that collects and stores solar energy. Solar ponds do not use tracking systems such as mirrors, nor do they concentrate the Sun's rays like many other solar energy technologies.

There are two types of convection solar ponds. (Convection is a process in which a fluid such as water circulates, and in so doing, the circulation causes a transfer of heat.) One is called a salt-gradient pond. At the very bottom of the pond is a dark layer that can absorb heat. This is usually a liner made of butyl rubber or other dark material. In addition to helping the water absorb the heat, it helps protect the nearby soil and groundwater from being contaminated by the saltwater from the solar pond.

In the pond, there is a significant amount of salt located near the bottom. The types of salt commonly used are sodium chloride (NaCl) or magnesium chloride (MgCl_2). The water is saturated (filled entirely) or almost saturated with salt. The closer to the surface, the less salt is found in the water. At the very top of the pond is a layer of freshwater (that is, water without salt). This change in saltiness forms layers in the pond. The gradual change in the amount of salt is called a salt-density gradient.

The layers of saltwater stop the natural tendency of hot water to rise to the surface. Thus, the water that is heated by the Sun stays at the bottom of a solar pond. The layers that are close to the surface remain cool. There is a significant temperature difference between the top and the bottom of a solar pond, though some heat can be stored on every layer. Temperatures as high as 82 to 93°C (179 to 199°F) can be found at the bottom. The heat is extracted by a heat exchanger at the bottom of the pond. This heat energy can power an engine, provide space heating, or produce electricity via a low-pressure steam turbine. The heated saltwater can be pumped to the location where the heat is needed. After the heat is used, the water can be returned to the solar pond and heated again.

The second type of convection pond is a membrane pond. A membrane pond is similar to the salt-gradient pond except the layers of water are physically divided. They are separated by membranes that are thin and transparent. The separation of layers physically prevents convection (circulating movement). With a membrane pond, the heat that is created is also removed from the bottom layer of the pond as in a salt-gradient pond.

There are also two types of non-convection ponds. One is called a shallow solar pond. This pond has no saltwater. Pure freshwater is kept inside a large bag. The bag allows convection to take place but limits the amount of water that can be evaporated. At the bottom of the bag is a black area. Foam insulation can also be found near the bottom. On top of the bag are two types of glazing which are typically sheets of plastic or glass.

In a shallow solar pond, the sunshine heats the bag and the water inside during the day. The heat energy is extracted at night. The heated water is pumped into a large heat storage tank. This process can be difficult because heat loss is possible. The problems with heat loss have meant that shallow solar ponds have not been fully developed as a technology.

See also: Solar Energy, Steam Turbine.

Solar Power

Solar power is often projected to be a potentially attractive alternative to fossil fuels. There are a number of special applications where solar power can be attractive, but for fundamental technological reasons, it is unlikely that it will be the ultimate solution for the electricity problems in various countries/regions.

Solar radiation may be converted directly into electricity by solar cells (photovoltaic cells). In such cells, a small electric voltage is generated when light strikes the junction between a metal and a semiconductor (such as silicon) or the junction between two different semiconductors.

There are two main advantages of producing electricity from the Sun. First, the source of energy is clearly renewable and free. Second, neither CO₂ nor other harmful emissions are produced during the energy conversion process.

In this sense, solar power is attractive environmentally. The disadvantages of solar energy are similar to those of wind. First, the Sun obviously shines brightly only during periods of cloud-free daytime. Consequently, producing base load power is not possible since there is no simple way to store excess energy during the day for use at night. Second, the Sun's intensity is low compared to that in a coal furnace.

Therefore, a large area of solar cells is required to produce a significant amount of power. For example, an area of approximately 50 square miles would have to be covered by solar panels to provide the 2.4 GW required by Boston. Recall that the area of Boston is also approximately 50 square miles so that the useful measure of energy for solar power can be produced.

Thus, solar power faces some challenges if it is to be used to produce large quantities of electricity. There are other more attractive uses, such as for residential and some commercial heating.

See also: Photovoltaic Cells, Photovoltaics.

Solar Tower

A solar tower (also known as a power tower, a central receiver, or a heliostat mirror power plant) uses solar energy to generate enough power to provide electricity over a large area. In this system, the Sun's power is collected by a large field of flat, movable mirrors. Sometimes, there are thousands of mirrors. The mirrors, called heliostats, move so they can track the Sun. They are focused on one single, fixed receiver that is located on top of a tall, central tower. Temperatures can be produced from 550 to 1,500°C (1,020 to 2,730°F) at the receiver.

The receiver collects all the energy and heat into a heat-transfer fluid that is flowing through it. In early power towers, this fluid was plain water. However, more recent models usually use molten salt, though liquid sodium, nitrate salt, and oil are also used. The heat energy held in the salt is used to boil water and make steam. This steam is used to generate electricity in a steam generator, usually located at the foot of the tower.

Molten salt can act as an efficient thermal storage medium for the heat collected in the solar tower. The heat can be stored for many hours or several days in this fashion. This storage medium is important. It allows the solar towers to be operational for up to 65% of the year. The rest of the time, a backup fuel source is used. When there is no energy storage medium, solar towers can only be used for approximately 25% of the year.

Solid Bed Adsorption

The solid bed adsorption process uses adsorbents that have the capability to adsorb high-boiling hydrocarbon derivatives from gas streams. The adsorbent may be silica gel or activated charcoal. Activated alumina cannot be used in the presence of high-boiling hydrocarbon derivatives, which foul the adsorbent.

The design of an adsorbent-based system for high-boiling hydrocarbon removal is more complicated than that of a system for the removal of water only. For instance, different grades of adsorbent may be required, and the system must also be designed to accommodate the adsorption of more than one component.

The adsorption process is continuous with respect to the gas but cyclical with respect to the adsorbent bed because the latter must be regenerated when it becomes saturated with condensate. Regeneration is accomplished by passing heated recycle gas through the bed. The condensate is recovered from the regeneration gas by cooling, condensation, and phase separation. To recover a large fraction of the hydrocarbon derivatives, while limiting the volume of adsorbent, it is preferable to use a relatively short cycle time, approximately one hour. In practice, this cycle time may vary within a fairly wide interval, between twenty minutes and several hours, depending on the quality of the hydrocarbon gas.

This process is appropriate for relatively low concentrations of high-boiling hydrocarbon derivatives. It can be also appropriate if the gas is at a high pressure, close to the cricondenbar. In this case, refrigeration processes become ineffective and separation by adsorption may offer the only way to obtain the required specifications.

The adsorption processes are easy to start up and to operate at high turn-down (changes in throughput), and so are useful for variable and on-stream and off-stream operations.

See also: Adsorption, Gas Cleaning, Gas Processing, Gas Treating.

Solid Desiccant Dehydration

A solid desiccant is a hygroscopic solid material that is used to induce or sustain a state of dryness (desiccation) in its vicinity; it is the opposite of a humectant. Desiccants for specialized purposes may be in forms other than solid, and may work through other principles, such as chemical bonding of water molecules. They are commonly encountered in foods to retain crispness. Industrially, desiccants are widely used to control the level of water in gas streams.

Although some desiccants are chemically inert, others are extremely reactive and require specialized handling techniques. The most common desiccant is silica (SiO_2), an otherwise inert, nontoxic, water-insoluble white solid. Tens of thousands of tons are produced annually for this purpose. Other common desiccants include activated charcoal, calcium sulfate (CaSO_4), calcium chloride (CaCl_2), and molecular sieves (typically a zeolite derivative).

Some desiccants are only suitable for dehydrating the gas while others are capable of performing both dehydration and removal of high-boiling hydrocarbon components. The selection of proper desiccant for a given application is a complex problem. For solid desiccants used in gas dehydration, the following properties are desirable: (i) high adsorption capacity at equilibrium, which lowers the required adsorbent volume, allowing for the use of smaller vessels with reduced capital expenditures and reduced heat input for regeneration, (ii) high selectivity, which minimizes the undesirable removal of valuable components and reduces overall operating expenses, (iii) easy regeneration in which the relatively low regeneration temperature minimizes overall energy requirements and operating expenses, (iv) low pressure drop, (v) good mechanical properties (such as high crush strength, low attrition, low dust formation, and high stability against aging) which lower the overall maintenance requirements by reducing the frequency of adsorbent change out and minimizing downtime-related losses in production, and (vi) cheap, non-corrosive, non-toxic, chemically inert, high bulk density and no significant volume changes upon adsorption and desorption of water.

The most common commercial desiccants used in dry-bed dehydrators are molecular sieves and silica gel. However, a molecular sieve is the most versatile adsorbent because it can be manufactured for a specific pore size, depending on the application. The sieve should be (i) capable of dehydration to less than 1 ppm water content, (ii) the overwhelming choice for dehydration prior to cryogenic processes (especially true for LNG), and (iii) excellent for hydrogen sulfide removal, carbon dioxide removal, dehydration, high temperature dehydration, high-boiling hydrocarbon liquids, and highly selective removal. Molecular sieves, however, are more expensive than silica gel, but offer greater dehydration and require higher temperatures for regeneration, thus higher operating cost.

Silica gel is a widely used desiccant and is characterized by the following: (i) well suited for normal dehydration of natural gas, (ii) easily regenerated than molecular sieves, (iii) has high water capacity, where it can adsorb up to 45% of its own weight in water, (iv) costs less than molecular sieve. However, whatever the qualities, no desiccant is perfect or best for all applications. In some applications, the desiccant choice is determined primarily by economics. In other cases, the process conditions control the desiccant choice.

In the dehydration cycle, the wet inlet gas flows downward through the tower. The adsorbable components are adsorbed at rates dependent on their chemical nature, the size of their molecules, and the size of the pores in the solid material. The water molecules are adsorbed first in the top layers of the desiccant bed. Dry hydrocarbon gases are adsorbed throughout the bed. As the upper layers of desiccant become saturated with water, the water in the wet gas stream begins displacing the previously adsorbed hydrocarbon derivatives in the lower desiccant layers. Liquid hydrocarbon derivatives will also be absorbed and will fill pore spaces that would otherwise be available for water molecules. For each component in the inlet gas stream, there will be a section of bed depth, from top to bottom, where the desiccant is saturated with that component and where the desiccant below is just starting to adsorb that component.

The depth of bed from saturation to initial adsorption is known as the mass transfer zone (MTZ). This is simply a zone or section of the bed where a component is transferring its mass from the gas stream to the surface of the desiccant. As the flow of gas continues, the mass transfer zone moves downward through the bed and water displaces the previously adsorbed gases until finally the entire bed is saturated with water vapor. When the leading edge of the mass transfer zone reaches the end of the bed, breakthrough occurs. If the entire bed becomes completely saturated with water vapor, the outlet gas is just as wet as the inlet gas. Obviously, the towers must be switched from

the adsorption cycle to the regeneration cycle (heating and cooling) before the desiccant bed is completely saturated with water.

At any given time, at least one of the towers will be adsorbing while the other towers will be in the process of being heated or cooled to regenerate the desiccant. When a tower is switched to the regeneration cycle, some wet gas (that is, the inlet gas downstream of the inlet gas separator) is heated to temperatures of 230 to 315°C (450 to 600°F) in the high-temperature heater and routed to the tower to remove the previously adsorbed water. As the temperature within the tower is increased, the water captured within the pores of the desiccant turns to steam and is absorbed by the natural gas. This gas leaves the top of the tower and is cooled by the regeneration gas cooler. When the gas is cooled, the saturation level of water vapor is lowered significantly and water is condensed. The water is separated in the regeneration gas separator, and the cool, saturated regeneration gas is recycled to be dehydrated. This can be done by operating the dehydration tower at a lower pressure than the tower being regenerated or by recompressing the regeneration gas. Once the bed has been “dried” in this manner, it is necessary to flow cool gas through the tower to return it to normal operating temperatures (approximately 38 to 49°C, 100 to 120°F) before placing it back in service to dehydrate gas. The cooling gas could either be wet gas or gas that has already been dehydrated. If wet gas is used, it must be dehydrated after being used as cooling gas, where a hot tower will not sufficiently dehydrate the gas.

Bed switching is controlled by a time controller that performs switching operations at specified times in the cycle. The length of the different phases can vary considerably. Longer cycle times will require larger beds, but will increase the bed life. A typical two-bed cycle might have an eight-hour adsorption period with six hours of heating and two hours of cooling for regeneration. The 16 hours adsorption time for an adsorption unit with three beds, two beds in adsorption, and one bed in regeneration also makes a full cycle time of 24 hours.

Internal or external insulation for the adsorbers may be used. The main purpose of internal insulation is to reduce the total regeneration gas requirements and costs (invest cost however is higher). Internal insulation eliminates the need to heat and cool the steel walls of the adsorber vessel. Normally, a castable refractory lining is used for internal insulation. The refractory must be applied and properly cured to prevent liner cracks. Liner cracks will permit some of the wet gas to bypass the desiccant bed. Only a small amount of wet, bypassed gas is needed to cause freeze-up in cryogenic plants. Ledges installed every few feet along the vessel wall can help eliminate this problem.

See also: Adsorption, Gas Cleaning, Gas Processing, Gas Treating.

Solid Emissions

The non-volatile oxidation products of the inorganic constituents of the fuel (e.g., sodium, potassium) are left as ash and contribute to the formation of corrosive deposits. When pulverized coal is used, a large proportion of the ash is carried out of the combustion chamber with the exhaust gas stream and has to be removed as completely as possible, usually by use of electrostatic precipitators. The removal of fly ash from combustion effluent streams is as important to the environment as the removal of sulfur oxides and nitrogen oxides. If not removed, the inorganic constituents and the organic constituents of the ash can cause serious environmental consequences, in addition to the solid particles acting as condensation nuclei and (catalytic) surfaces for the conversion of sulfur dioxide to the trioxide:



Because of its organic origin and its intimate co-mixture with mineral formations, coal contains a large number of elements in minor or trace quantities. Of the known non-transuranic elements, only a minority has not yet been found in coal. In regard to the behavior of trace elements in coal-fired power plants, the elements have been divided into two groups, those appearing mainly in the bottom ash (elements or oxides having lower volatility) and those appearing mainly in the fly ash (elements or oxides having higher volatility). For power plants using dry particulate collection devices, such as electrostatic precipitators, it was believed that the most volatile elements (such as mercury and selenium) could actually escape in the elemental state with the flue gas; wet scrubbers, however, were believed capable of removing most of the elements from the gas streams and transferring them to the liquid effluent. Essentially no particulates from coal combustion should be ejected into the atmosphere; all particulate streams

should be collected and either returned to the combustors, where they melt and are removed as slag, or are removed as fly ash. Any eventual dispersion of the elements present depends on the possibility of leaching. The concern, therefore, is to identify elements that may be occurring in the gaseous state. Among the trace elements present in coal with recognized toxic properties, high-volatility elements (beryllium, mercury, and lead) do not form gaseous-hydrides, will condense on cooling and likely will be almost completely removed by the aqueous condensates formed on gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous hydrides, (covalent) hydrides such as arsine (AsH_3), stibine (SbH_3), and hydrogen selenide (H_2Se). These however, have stability characteristics that preclude their formation at the temperature and pressure prevailing in the oil/gas plant gasifiers.

Solid Fuels

Solid fuels are those fuels that are solid under ambient conditions and remain solid under mild heating. Thus, examples of solid fuels from biofuel feedstocks include wood and wood-derived charcoal and dried dung, particularly cow dung.

Compared to gaseous fuels and liquid fuels, solid fuels are often cheaper, easier to extract, more stable to transport, and in many places are more readily available. In particular, coal is utilized in the generation of electricity because it is less expensive and more powerful than its gaseous or liquid fuel counterparts. However, solid fuels are also heavier to transport, require more destructive methods to extract/burn, and often have higher carbon, nitrate, and sulfate emissions. With the exception of sustainable wood/biomass, solid fuel (such as peat or coal) is typically considered to be non-renewable because it requires thousands of years to form.

One widespread use of such fuels is in home cooking and heating. The biofuel may be burned on an open fireplace or in a special stove. The efficiency of this process may vary widely, from 10% for a well-made fire (even less if the fire is not made carefully) up to 40% for a custom-designed charcoal stove. Inefficient use of fuel is a cause of deforestation (though this is negligible compared to deliberate destruction to clear land for agricultural use), but more importantly, it means that more work has to be put into gathering fuel, thus the quality of cooking stoves has a direct influence on the viability of biofuels.

See also: Biofuel, Biomass, Solid Fuels from Waste.

Solid Fuels from Waste

The use of organic waste as cooking fuel in both rural and urban areas is not new. In seventeenth-century England, the rural poor often burned dried cow dung because of the acute shortage of wood fuel due to widespread deforestation. In some countries, cattle and buffalo dung is still used as relatively good cooking fuel. In the beginning of the nineteenth century, sawdust briquettes were made with binding materials such as tar, resins, and clay bind the small particles together. None of these processes attained great importance because of their relatively high costs compared to wood and conventional charcoal fuels.

Fuel briquettes emerged as a significant business enterprise in the 20th century. In the 1950s, several economic methods were developed to make briquettes without a binder. A multitude of factories throughout the world produced literally tens of millions of tons of usable and economic material that met the household and industrial energy needs. During the two World Wars, households in many European countries made their own briquettes from soaked waste paper and other combustible domestic waste using simple lever-operated presses. Modern industrial briquetting machines, although much larger and more complex, operate on the same principle.

Briquetting is undergoing resurgence, principally due to the convergence of three critical factors. First, the recent developments in briquette processing and binding have dramatically changed the economics of using fuel briquettes as an energy resource. Secondly, a shortage of fuel wood has become increasingly severe in most of the developing countries. Finally, there has been a steady increase by environmental concerns to address the problem of domestic and urban waste disposal, a dilemma that briquetting can help remedy.

See also: Bagasse Briquettes, Briquetting, Urban Waste Briquettes.

Solid Fuels from Wood

Burning wood as a fuel is the largest current use of wood-derived energy. Wood can be used in many forms as a solid fuel for cooking or heating, occasionally for steam engines, and for steam turbines that generate electricity.

The use of wood as a fuel source heat energy is as old as civilization itself. Historically, it was limited in use only by the distribution of technology required to make a spark. Wood heat is still common throughout much of the world, although it has been mainly replaced with coal, oil, or natural gas heating. Wood heating has been singled out as a serious health hazard in many regions of the world.

Early examples include the use of wood heat in tents. Fires were constructed on the ground, and a smoke hole in the top of the tent allowed the smoke to escape by convection. In permanent structures, hearths were constructed – surfaces of stone or another noncombustible material upon which a fire could be built. Smoke escaped through a smoke hole in the roof. The development of the chimney and the fireplace allowed for more effective exhaustion of the smoke. Masonry heaters or stoves went a step further by capturing much of the heat of the fire and exhaust in a large thermal mass, becoming much more efficient than a fireplace alone.

The particular form of wood fuel used depends upon (among other things) its source, quantity, and quality. Available forms include logs, bolts, blocks, firewood, stove-wood (often from split blocks), charcoal, chips, sheets, pellets, and sawdust. Sawmill waste and construction industry by-products also include various forms of lumber tailings.

See also: Fuel Wood, Logs and Wood Chips, Pellets and Briquettes, Steam Turbine.

Solid Waste

Solid waste is any garbage, refuse, sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility and other discarded materials including solid, liquid, semi-solid, or contained gaseous material, resulting from industrial, commercial, mining and agricultural operations, and from community activities. Solid waste does not include solid or dissolved materials in domestic sewage, or solid or dissolved materials in irrigation return flows or industrial discharges. Also, a material cannot be a hazardous waste if it does not meet the definition of solid waste. Thus, wastes that are excluded from the definition of solid waste are not subject to hazardous waste regulation.

Generation of such wastes is typically originated from the residential community (i.e., municipal solid waste, MSW) or from commercial and light-industrial communities. Wastes generated from manufacturing activities of heavy-industrial and chemical industries involve wastes that are typically classified as hazardous wastes. As regulations continue to get stricter with decreasing land availability, alternative uses for the waste must be found in order to recover the residual heating values as well as to alleviate landfill-overburdening problems.

In landfill, the biodegradable components of the municipal solid waste decompose over time and emit methane – a very potent greenhouse gas that is known to be 23 times more potent than carbon dioxide as greenhouse gas. Therefore, the biodegradable components in municipal solid waste such as food and paper wastes that end up with going to landfills must be reduced in order to practice a good waste management plan. While refuse-derived fuel (RDF) is attractive from the sense of resource conservation as well as waste reduction, it also causes some serious concerns that the waste treatment for energy generation may result in new forms of environmental problems. Most of the processing difficulties arise from the heterogeneous and non-uniform nature of the waste feed itself which, in turn, generates a very widely varying spectrum of treated intermediates and by-products.

See also: Refuse-Derived Fuel, Municipal Solid Waste, Waste.

Solvent Extraction

Solvent extraction is a commonly used method to recover valuable materials or to remove contaminants from aqueous or non-aqueous waste streams. Leaching is solvent extraction applied to solid feeds. Solvent extraction is usually physical process in which selectivity is dependent on the relative solubility of the feedstock components in a chosen solvent.

The solvents used for solvent extraction can be either conventional liquids below their critical point or supercritical fluids operating at conditions above the critical point of the pure solvent. Most, if not all, of the separations that can be made with supercritical fluid solvents can also be made with liquid solvents. However, in some specific applications, there are enough operating benefits to favor supercritical fluids. Examples of these benefits are (i) lower operating temperature for heat-sensitive materials, (ii) ease of solvent recovery by pressure reduction or temperature increase, and (iii) faster phase separation due to lower viscosities and higher density differences between phases. The trend is toward increased use of supercritical fluid extraction solvents.

The interaction between solvent and solute can be purely physical intermolecular attraction, or there may be additional chemical forces superimposed on the physical attraction. These chemical forces increase the solvent selectivity for the materials that interact chemically with the solvent. They are the basis for extracting polar organics, metals, and ionic materials from aqueous streams. Examples of such interactions are ionic bonding, hydrogen bonding, and chemical complexing. The extraction processes using ionic interactions are frequently called liquid ion exchange.

In contrast to liquid extraction, which extracts a dissolved material from a liquid feed into a solvent, solvent precipitation works by dissolving an antisolvent into the liquid feed. This results in the formation of a second liquid or solid phase insoluble in the feed. The same fundamentals governing solubility of liquids in each other apply to both solvent extraction and solvent precipitation.

Solvent extraction is usually applied to liquid feeds. It is then called liquid-liquid extraction or supercritical fluid extraction. However, it can also be applied to solids and sludges to remove soluble liquid or solid impurities which permits both the recovery of valuable materials and the regeneration of solid adsorbents and catalysts. This type of extraction is usually referred to as leaching.

See also: Liquid-Liquid Extraction, Recovery Processes, Solvent Extraction., Supercritical Fluid Extraction.

Solvent Precipitation

Solvent precipitation differs from conventional liquid-liquid extraction in that the added solvent is not selectively dissolving the impurities but is changing the solvent properties of the feed so that the impurities can no longer stay in solution. The added solvent dissolves in the carrier of the waste contaminants and precipitates the impurities by generating a new carrier solvent which cannot hold the impurities in solution. The impurities then precipitate out of solution to form a second liquid phase or a solid phase.

Solvent precipitation techniques are based on the concept that high-molecular-weight and/or highly polar materials such as asphaltenes would normally not dissolve in oil. However, they are held in solution as a colloid by intermediate peptizing agents which interact strongly with the high-molecular-weight polar compounds. In the process, the most polar, highest-molecular-weight fractions precipitate first, followed by less polar and lower-molecular-weight fractions as the quantity of precipitating agent is increased. The precipitate can be either a solid or a liquid depending on the melting and solution properties of the precipitate.

See also: Liquid-Liquid Extraction, Recovery Processes, Solvent Extraction., Supercritical Fluid Extraction.

Sorghum

Sorghum is an annual tropical grass with large genetic variation that is a crop with the potential for energy production. It is a genus of flowering plants in the grass family Poaceae. Seventeen of the 25 species are native to Australia with the range of some extending to Africa, Asia, and Central America as well as to islands in the Indian Ocean and the Pacific Ocean. One species is grown for grain, while many others are used as fodder plants, either cultivated in warm climates throughout the world or naturalized, in pasture lands.

Sweet sorghum has been selected for its sugar content and is normally grown for molasses production. Forage sorghum has been selected for high yields of reasonably good-quality animal feed. Sorghum varieties producing tall plants with large stems make the best candidates for biomass production. Both sweet and forage sorghum have a high potential for lodging. Lodging can result in harvest problems with ensuing loss of yield from both initial and ratoon crops.

This crop has been cultivated on a small scale in the past for production of table syrup, but other varieties can be grown for production of sugar. The most common types of sorghum species are those used for production of grain. Sweet sorghum can be considered as an energy crop, because it can be grown in all continents, in tropical, sub-tropical, temperate regions as well as in poor-quality soils. Sweet sorghum is a warm-season crop that matures earlier under high temperatures and short days. Sweet sorghum is an extraordinarily promising multifunctional crop not only for its high economic value but also for its capacity to provide a very wide range of renewable energy products, industrial commodities, food, and animal feed products. Sweet sorghum biomass is rich in readily fermentable sugars, and thus it can be considered as an excellent raw material for fermentative hydrogen production – hydrogen is an important commodity for the refining industry, and new sources are continually sought. Integrated production of several crops (sweet sorghum/sugar-cane/sweet sorghum corn/sweet sorghum/sweet potatoes) and simultaneous processing of the full crop components (starch, sugar, lignocellulosic) can improve the global economics of bioenergy schemes considerably in view of a viable production of bioethanol.

Sweet sorghum crops produce sugar syrups which could form the basis of fermentation processes for methane or ethanol production, and some of the forage types of the plant may be suitable for biomass production. Sweet sorghum has been grown in the southern United States for making syrup for many years and several widely adapted, high-yielding cultivars with high sugar concentrations are available. Sorghum production and harvesting can be completely mechanized with currently available equipment, and the juice can be fermented directly without enzyme treatment or cooking.

The economics of production and processing could offset the lower alcohol-yielding potential. An additional advantage to sorghum is that the crushed stalks make good-quality silage which could be used to winter cattle. The primary disadvantage of sorghum is that juice cannot be stored without refrigeration; therefore, use of sorghum as a feedstock is probably limited to a 2- or 3-month harvest period in the late summer and fall.

See also: Cordgrass, Grasses, Switchgrass.

Sour Gas

Sour gas is any gas stream that contains significant amounts of hydrogen sulfide (H_2S). Natural gas is usually considered sour if there are more than 5.7 milligrams of hydrogen sulfide per cubic meter of natural gas, which is equivalent to approximately 4 ppm v/v. A gas stream that does not contain significant amounts of hydrogen sulfide is generally referred to as sweet gas.

Although the terms acid gas and sour gas are used interchangeably, strictly speaking, a sour gas is any gas that contains hydrogen sulfide in significant amounts, whereas an acid gas is any gas that contains significant amounts of acidic gases such as carbon dioxide (CO_2) or hydrogen sulfide. Thus, carbon dioxide by itself is an acid gas, but it is not a sour gas.

Before a raw gas stream containing hydrogen sulfide and/or carbon dioxide can be used, the raw gas must be treated to remove those impurities to acceptable levels, commonly by an amine gas treating process. The removed hydrogen sulfide is most often subsequently converted to by-product elemental sulfur in a Claus process, or it can be treated in a wet sulfuric acid process unit where the by-product is sulfuric acid.

Processes that are designed to remove mercaptans and/or hydrogen sulfide are commonly referred to as sweetening processes because they result in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide. Hydrogen sulfide is a toxic gas. It also places restrictions on the materials that can be used for piping and other equipment handling sour gas, as many metals are sensitive to sulfide stress cracking. The presence of hydrogen sulfide in gas causes lower-quality burning, and the production of sulfur dioxide, and so is regulated in commercially sold gas.

See also: Gas Cleaning, Gas Processing, Gas Treating, Natural Gas, Refinery Gas.

Soybeans

Soybeans (soyabeans) are a bushy, leguminous plant, *Glycine max*, native of South-East Asia that is grown for the beans, which are used widely in the food industry, for protein in cattle feed and for oil production.

Soybeans are the most commonly grown oil seed crop in the Southeastern United States and the easiest to grow and harvest. Yields are quite dependent on rainfall and various management factors including crop rotation and double-cropping with wheat. It is not particularly difficult to produce in excess of 3,000 kg/ha in a good year with an adapted cultivar. While soybeans produced less oil than several of the other crops that were tested, the high protein content of the oil seed meal makes it a valuable by-product. The crop also has the advantage of being a legume and thus requires no nitrogen fertilizer.

Oil (approximately 40% w/w) and protein (approximately 20% w/w) content account for the majority of dry soybeans. The remainder consists of 35% carbohydrate (approximately 35% w/w) and mineral constituents (approximately 35% w/w).

The principal soluble carbohydrates of mature soybeans are the disaccharide sucrose (range 2.5 to 8.2% w/w), the trisaccharide raffinose (0.1 to 1.0%) composed of one sucrose molecule connected to one molecule of galactose, and the tetra-saccharide stachyose (1.4 to 4.1%) composed of one sucrose molecule connected to two molecules of galactose.

The higher-molecular-weight insoluble carbohydrates in soybeans consist of the complex polysaccharides cellulose, hemicellulose, and pectin.

To extract soybean oil from seed, the soybeans are cracked, adjusted for moisture content, rolled into flakes, and solvent-extracted with commercial hexane. The oil is then refined, blended for different applications, and sometimes hydrogenated. Soybean oils, both liquid and partially hydrogenated, are exported abroad, sold as vegetable oil, or end up in a wide variety of processed foods. The remaining soybean husks are used mainly as animal feed.

Biodiesel from soybean oil can be used in diesel engines with little or no modifications. The transesterification process gives two products: biodiesel and glycerin (used to make soap).

As compared to normal diesel, soy biodiesel is better for the environment because it is made from renewable resources and has lower emissions compared to diesel fuel from crude oil. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbon derivatives, carbon monoxide, and soot. The use of biodiesel does not increase the carbon dioxide level in the atmosphere, since growing soybeans also consumes carbon dioxide. Biodiesel is also more biodegradable than conventional diesel, and lubrication tests have demonstrated the lubrication advantage of biodiesel.

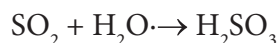
See also: Biodiesel, Diesel Fuel, Transesterification.

SO_x

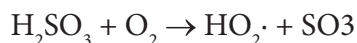
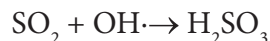
SO_x is the shortened version for the term *oxides of sulfur* which are emitted when a sulfur-containing fuel is combusted.

Sulfur oxides (SO_x) are compounds of sulfur and oxygen molecules. Sulfur dioxide (SO₂) is the predominant form found in the lower atmosphere. It is a colorless gas that has a pungent, unpleasant odor. Sulfur dioxide dissolves readily in water present in the atmosphere to form sulfurous acid (H₂SO₃). Approximately 30% of the sulfur dioxide in the atmosphere is converted to sulfate aerosol (acid aerosol), which is removed through wet or dry deposition processes. Sulfur trioxide (SO₃), another oxide of sulfur, is either emitted directly into the atmosphere or produced from sulfur dioxide and is rapidly converted to sulfuric acid (H₂SO₄).

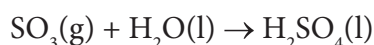
When atmospheric pollutants such as sulfur dioxide and nitrogen oxides mix with water vapors in the air, they are converted to sulfurous acid:



In the gas phase, sulfur dioxide is oxidized by reaction with the hydroxyl radical via an intermolecular reaction:



In the presence of water, sulfur trioxide (SO₃) is converted rapidly to sulfuric acid:



Acid rain (acid deposition) can be classified as wet deposition such as acid rain, snow, sleet, and fog or dry deposition such as deposition as particulate matter even less than PM 2.5. The effects of acid rain can either be chronic or episodic. Chronic acidification is a long-term effect due to years of acid rain. Episodic acidification is due to heavy rain storms; it also occurs in spring as concentrated nitrate and sulfate in the lower layer of snow pack get released when snow melts. A second method of acid deposition is known as dry deposition. While wet deposition involves the precipitation of acids, dry deposition occurs when the acids are first transformed chemically into gases and salts, before falling under the influence of gravity back to Earth. Sulfur dioxide, for example, is deposited as a gas and as a salt.

See also: Acid Rain.

Specific Gravity

The specific gravity is the mass (or weight) of a unit volume of any substance at a specified temperature compared to the mass of an equal volume of pure water at a standard temperature. Substances with a specific gravity greater than one are denser than water, and so will sink in it, and those with a specific gravity of less than one are less dense than water, and so will float in it.

Specific gravity, SG, is expressed mathematically as:

$$\text{Specific gravity} = (\text{density of substance})/(\text{density of water})$$

Since the density of water varies with temperature and pressure, it is usual to refer specific gravity to the density at 4°C (39.2°F) and a normal pressure of 1 atmosphere. The given temperature and pressure are preferred because it is when water has its maximum density. In this case, the density of water is equal to 1,000 kg·m⁻³ in SI units (or 62.43 lb per cubic foot, 62.43 lb·ft⁻³ in the customary units of the United States). Given the specific gravity of a substance, its actual density can be calculated by inverting the above formula:

Density of the substance = specific gravity x (density of water)

Occasionally, a reference substance other than water is specified (for example, air), in which case specific gravity means density relative to that reference.

In addition, the specific gravity of gas can also be determined and is defined as:

$$\text{Specific gravity of gas} = M/M_{\text{air}}$$

M_{air} is the molecular weight of air, which is equal to 29. Once we can calculate the value of the molecular weight of the mixture, we can calculate the specific gravity of the mixture. For a gas mixture, the molecular weight can be calculated as:

$$M = \sum_{i=1}^n y_i M_i$$

M_i is the molecular weight of component i , y_i is the mole fraction of component i , and n is the total number of components.

Specific Heat

Specific heat is the quantity of heat required to raise a unit mass of material through one degree of temperature (ASTM D2766). Specific heats are extremely important engineering quantities in refinery practice because they are used in all calculations on heating and cooling petroleum products. Many measurements have been made on various hydrocarbon materials, but the data for most purposes may be summarized by the general equation:

$$C = 1/d (0.388 + 0.00045t)$$

C is the specific heat at t°F of an oil whose specific gravity 60/60°F is *d*; thus, specific heat increases with temperature and decreases with specific gravity.

Spontaneous Combustion

Spontaneous combustion is the self-ignition of carbonaceous material through oxidation under specific conditions. Different types of material in the tendency toward self-ignition. Spontaneous combustion is usually the culmination of several separate chemical and physical events. It is a question of degree and the correct order of reactions being in place.

In ordinary combustion, the material is deliberately heated to its ignition point to make it burn. During this process, many materials (especially hydrocarbon derivatives) undergo slow oxidation that, like the rapid oxidation of burning, releases heat. If the heat so released cannot escape, the temperature of the hydrocarbon rises until ignition takes place. Spontaneous combustion often occurs in piles of hydrocarbon-soaked (oily) rags and can constitute a serious fire hazard. Also, fires started by spontaneous combustion are caused by the following mechanisms: (i) spontaneous heating, (ii) pyrophoricity, and (iii) hypergolic reactions.

Spontaneous heating is the slow oxidation of an element or compound which causes the bulk temperature of the element or compound to rise without the addition of an external heat source. Spontaneous heating may be the result of direct oxidation of hydrocarbons (for example, oils and solvents), or it may occur because of the action of microorganisms in organic materials. Saturated hydrocarbon derivatives (such as alkane derivatives) do not have a tendency for spontaneous combustion, whereas unsaturated hydrocarbons do have a tendency for spontaneous combustion.

Pyrophoric substances are substances (or chemicals) that ignite instantly upon exposure to air (atmospheric oxygen). A pyrophoric substance may be a solid, liquid, or gas. Most materials are not pyrophoric unless they are in a very finely divided state. Although there are some pyrophoric liquids and gases, most pyrophoric materials are metals. Pyrophoricity is a special case of a hypergolic reaction because the oxidizing agent is restricted to atmospheric oxygen.

A *hypergolic reaction* describes the tendency of a material ability to spontaneously ignite or explode upon contact with any oxidizing agent. Some hydrocarbons are capable of spontaneous heating and ignition under proper conditions. Spontaneous heating of hydrocarbons usually involves a combustible liquid hydrocarbon in contact with combustible materials. An example of this would be combustible rags impregnated with oils or solvents. Whether or not spontaneous heating leads to ignition depends on several items: (i) the rate at which heat is generated and removed from the material being oxidized, (ii) the ignition temperature of the fibrous combustible material, hydrocarbon, or any gases liberated by oxidation, (iii) the specific area (cm²/g, defined below) of the hydrocarbon exposed to an oxidizer, and (iv) the amount of moisture present in the atmosphere and the fibrous material.

Spontaneous combustion may occur in piles of moist organic material where heat is generated in the early stages by the respiration of bacteria, molds, and microorganisms. High moisture content is required for vigorous activity, and heating is generally controlled by maintaining the moisture content below a predetermined level. This type of heating can only raise the material to the temperature range of 50 to 75°C (122 to 167°F), where the living organisms die.

Beyond this point, the oxidant of the material must take over if ignition is to occur. The existence of biological heating requires careful control of moisture, air supply, and nearby combustible or flammable materials. If a hot spot in a pile of organic material comes in contact with a highly flammable liquid or gas, a fire or explosion may

occur. Heat generated by biological action may also act as a catalyst for other reactions which occur only at elevated temperatures.

See also: Spontaneous Ignition.

Spontaneous Ignition

Spontaneous ignition is the ignition of a fuel under normal atmospheric conditions; usually induced by climatic conditions. Spontaneous ignition is a possible cause of unwanted fire and involves the ignition of a combustible material by its own heat of reaction without external heat or other source of ignition.

Two basic factors contribute to spontaneous heating and ignition: heat generation and heat dissipation. If heat generates faster than it dissipates, it accumulates, i.e., temperature increases. Of the many kinds of heat-generating reactions, oxidation is the most common. Practically all organic substances and some inorganic ones will oxidize if exposed to the atmosphere and produce heat. Usually, the rate of oxidation is slow. Only materials that are self-heating have a significant rate.

Spontaneous ignition is usually the culmination of several separate chemical events, although precise knowledge of the phenomenon is still somewhat incomplete but is gradually becoming known and there are means by which the liability of a coal to spontaneously ignite can be tested.

For example, exposure of a fuel to air will bring about not only loss of moisture but also oxidation. The latter process, often referred to as auto-oxidation or autoxidation, commences when the coal reacts with oxygen (of the atmosphere). Both processes result in an alteration of the properties of the material.

Sawdust and wood chips self-heat much more readily than solid wood; in general, fibrous and finely divided materials are more susceptible to spontaneous ignition. One reason is that a material in a finely divided state has a lower thermal conductivity than one in the solid state so that heat is accumulated more easily. Another is that any decrease in particle size results in increased surface area. An oxidation reaction takes place on the surface exposed to the air. Powdered metals such as aluminum and magnesium powders are much more easily ignited than solid metals.

Charcoal and carbon black are also susceptible to spontaneous ignition; the more finely divided the charcoal, the greater the hazard. Wood, when subjected to prolonged periods of heating and cooling cycles, may ignite spontaneously. The alternate heating and cooling processes may chemically decompose the wood to produce pyrophoric carbon, which oxidizes rapidly followed by ignition. Wood chips in huge piles, as at paper mills, are known to ignite spontaneously.

See also: Spontaneous Combustion.

Spray Tower

A spray tower consists of empty cylindrical or rectangular chambers in which the gas stream is contacted with liquid droplets generated by spray nozzles. A common form is a spray tower, in which the gas flows upward through a bank or successive banks of spray nozzles. Similar arrangements are sometimes used in spray chambers with horizontal gas flow. Such devices have low gas pressure drops, and all but a small part of the contacting power is derived from the liquid stream. The required contacting power is obtained from an appropriate combination of liquid pressure and flow rate.

Physical absorption depends on properties of the gas stream and liquid solvent, such as density and viscosity, as well as specific characteristics of the pollutant(s) in the gas and the liquid stream (e.g., diffusivity, equilibrium solubility). These properties are temperature dependent, and lower temperatures generally favor absorption of gases by the solvent. Absorption is also enhanced by greater contacting surface, higher liquid-gas ratios, and higher concentrations in the gas stream (EPA, 1991). Chemical absorption may be limited by the rate of reaction, although the rate-limiting step is typically the physical absorption rate, not the chemical reaction rate. Countercurrent packed towers are also used but, in some cases, they have a tendency to become plugged by collected particles or to scale when lime (CaO) or limestone (CaCO₃) scrubbing slurries are used.

Water is the most common solvent used to remove inorganic contaminants. Pollutant removal may be enhanced by manipulating the chemistry of the absorbing solution so that it reacts with the pollutant. An example of this is using caustic solution for acid-gas absorption instead of pure water as a solvent. Amphiphilic block copolymers dissolved in the water can be used to remove hydrophobic volatile organic compounds, which has much less affinity for water than hydrophilic volatile organic compounds. Used in flue gas desulfurization systems, spray tower scrubbers introduce a reagent slurry as atomized droplets through the spray nozzles at the top of, or in stages within the scrubber.

In the process, the gas (containing sulfur dioxide) enters at the bottom of the column and travels upward through the tower in a countercurrent flow, though horizontal spray towers which use a crosscurrent design also exist. In most cases, the sorbent is an alkaline slurry, commonly limestone (CaCO_3), slaked lime [$\text{Ca}(\text{OH})_2$], or a mixture of slaked lime and alkaline (typically potassium carbonate K_2CO_3 , or potassium bicarbonate, KHCO_3) fly ash, though many other sorbent processes exist. Absorption of sulfur dioxide is accomplished by the contact between the gas reagent slurry. The sulfur oxides react with the sorbent, forming a wet mixture of calcium sulfite (CaSO_3) and calcium sulfate (CaSO_4).

For horizontal flue gas desulfurization equipment process, the fresh slurry (composed of a recycle stream and a makeup stream) is often introduced at the last, or rear, stage of the absorber where the sulfur dioxide content of the gas stream is lowest. The slurry contacted in the last stage is pumped forward to the next stage. This way, the slurry flows countercurrent to the gas flow.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Spreading

Spreading is a form of dispersion in which the movement of chemical contaminants through the subsurface is complex and is difficult to predict since different types of chemicals react differently with soils, sediments, and other geologic materials and commonly travel along different flow paths and at different velocity. Chemicals released from a source area (typically on the surface) infiltrate (through solubility in water) into the subsurface and migrate downward by gravity as an aqueous solution through the vadose zone (the zone that extends from the top of the ground surface to the water table). When low permeability soil units are encountered, the contaminants in aqueous solution can also spread laterally along the permeability contrast.

Most chemical contaminants are introduced into the subsurface by percolation through soil strata, and the interactions between the soil and the chemical are important for assessing the fate and transport of the contaminant in the subsurface, especially in the groundwater system. Contaminants that are highly soluble, such as salts and any potentially ionic derivatives, can move readily from surface soil to saturated materials below the water table and often occurs during and after rainfall events. Those contaminants that may not be highly soluble may have considerably longer residence times in the surface strata (the soil zone). Some chemicals adsorb readily onto soil particles and slowly dissolve during precipitation events, resulting in migration into. Once below the water table, chemical contaminants are also subject to dispersion (mechanical mixing with uncontaminated water) and diffusion (dilution by concentration gradients). Many contaminants begin to spread immediately after entry into the environment.

See also: Absorption and Adsorption.

Stability and Instability

A fuel is a delicately balanced system insofar as the different fractions that contain hydrocarbon derivatives (saturates and aromatics) as well as heteroatom constituents. The heteroatom constituents tend to concentrate in the higher-molecular-weight fractions (the asphaltene constituents and resins). The nitrogen, oxygen, and sulfur species that are in near-neutral molecular locales will also occur in the saturate fraction and in the aromatics fraction, remembering that the nomenclature is not necessarily precise and that the composition of each fraction is a function of the separation process.

Instability (the formation of a separate or insoluble phase) usually occurs with the separation or precipitation of insoluble constituents. This may be caused by well stimulation, such as acidizing which involves a drastic shift in local chemical equilibria, pH, and liberation of carbon dioxide. It may also increase the concentration of some ions, such as iron, which will promote the formation of a sediment. Similarly, the separation of wax from paraffinic crude oil will also occur under certain conditions (some or defined, some are not) and cause problems during use by blocking the flow channels.

See also: Instability and Incompatibility.

Stabilization

Stabilization is the removal of relatively volatile constituents from a higher boiling fraction or product, or it is the production of a product which, to all intents and purposes, does not undergo any further reaction when exposed to the air.

The simplest stabilization process is a stripping process. Low-boiling naphtha from a crude tower, for example, may be pumped into the top of a tall, small-diameter fractional distillation tower operated under a pressure of 50-80 psi. Heat is introduced at the bottom of the tower by a steam reboiler. As the naphtha cascades down the tower, the light ends separate and pass up the tower to leave as an overhead product. Since reflux is not used, considerable amounts of liquid hydrocarbon derivatives pass overhead with the light ends.

An example of more precise stabilization can be seen in the handling of the mixture of hydrocarbon derivatives produced by cracking. The overhead from the atmospheric distillation tower that fractionates the cracked mixture consists of light ends and cracked naphtha with light ends dissolved in it. If the latter is pumped to the usual type of tank storage, the dissolved gases cause the naphtha to boil, with consequent loss of the gases and some of the liquid components. To prevent this, the naphtha and the gases dissolved in it are pumped to a stabilizer maintained under a pressure of approximately 100 psi and operated with reflux. This fractionating tower makes a cut between the highest boiling gaseous component (butane) and the lowest boiling liquid component (pentane). The bottom product is thus a liquid free of all gaseous components, including butane; hence, the fractionating tower is known as a debutanizer. The debutanizer bottoms (naphtha constituents) can be safely stored, whereas the overhead from the debutanizer contains the butane, propane, ethane, and methane fractions. The butane fraction, which consists of all the hydrocarbon derivatives containing four carbon atoms, is particularly needed to give easy starting characteristics to gasoline. It must be separated from the other gases and blended with motor gasoline in amounts that vary with the season: more in the winter and less in the summer. Separation of the butane fraction is effected by another distillation in a fractional distillation tower called a depropanizer, since its purpose is to separate propane and the lower-boiling gases from the butane fraction.

The depropanizer is similar to the debutanizer, except that it is smaller in diameter because of the smaller volume being distilled and is taller because of the larger number of trays required to make a sharp cut between the butane and propane fractions. Since the normally gaseous propane must exist as a liquid in the tower, a pressure of 200 psi is maintained. The bottom product, known as the butane fraction, stabilizer bottoms, or refinery casinghead, is a high-vapor-pressure material that must be stored in refrigerated tanks or pressure tanks. The depropanizer overhead, consisting of propane and lower-boiling gases, is used as a petrochemical feedstock or as a refinery fuel gas, depending on the composition.

Stack Gas

Stack gas is the product gas evolved during complete combustion of a fuel that is allowed to escape through a stack.

Combustion processes for heat and power generation and the incineration of household waste generate gaseous by-products that are not always adequate for the production of further products.

Flue gases from combustion facilities have a composition that is different from the composition of air because of high concentrations of the combustion products water (H_2O) and carbon dioxide (CO_2). More concern, however, goes to what is in these gases besides these bulk species, such as oxides of sulphur and nitrogen, fine dust,

trace elements such as mercury and nickel, and super-toxics such as dioxins. All of these compounds are actually unwanted by-products from a power plant or a waste incinerator, since the first has the objective to convert hydrocarbon fuels (C_xH_y) into carbon dioxide (CO_2), water (H_2O) plus heat and power, while the second aims at reducing a large volume of solid or liquid waste into a small amount of solid ashes plus, again, carbon dioxide and water from the combustion of the organic compounds. However, the fuel or waste materials that are combusted contain chemicals that are vaporized or converted chemically into gases that mix with the harmless gases water, carbon dioxide, oxygen, and nitrogen as, for example sulfur dioxide (SO_2), nitric oxide (NO), fly ash, and even hydrogen chloride when plastics (such as polyvinyl chloride) are combusted.

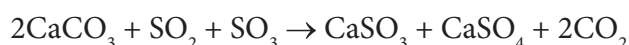
By means of a stack height, these gases (then known as stack gas(es)) can be dispersed into the atmosphere without much effect to the environment at short range. At the same time, the mere presence of a stack indicates that there must be reasons for actively transporting the gases away from the facilities that generate them. These reasons are that the temperature, and, more importantly, the composition of the gases are different from those of the ambient atmosphere at ground level. The formation of ground-level ozone from traffic exhaust gases during sunny summer days is a good example of what happens when large amounts of flue gases are released at ground level.

See also: Combustion.

Stack Gas Scrubbing

Most stack gas scrubbing processes are designed for sulfur dioxide removal; nitrogen oxides are controlled as far as possible by modification of combustion design and flame temperature regulation. However, processes for the removal of sulfur dioxide usually do remove some nitrogen oxides; particulate matter can be removed efficiently by commercially well-established electrostatic precipitators.

There are several processes for the removal of sulfur dioxide from stack gas, but scrubbing process utilizing limestone ($CaCO_3$) or lime [$Ca(OH)_2$] slurries have received more attention than other stack gas scrubbing processes. Attempts have been made to use dry limestone or dolomite ($CaCO_3 \cdot MgCO_3$) within the combustor as an *in situ* method for sulfur dioxide removal, thus eliminating the wet sludge from wet processes. This involves injection of dry carbonate mineral with the coal followed by recovery of the calcined product along with sulfite and sulfate salts:



The various solid products are removed by standard means, including cyclone separators and electrostatic precipitators.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Starch Crops

Starch (or *amylum*) is a polymeric carbohydrate consisting of numerous glucose units joined by glycosidic bonds called polymers.

The basic chemical formula of the starch molecule is $(C_6H_{10}O_5)_n$. Starch is a polysaccharide comprising glucose monomers joined in α 1,4 linkages. The simplest form of starch is the linear polymer amylose; amylopectin is the branched form. This polysaccharide is produced by most green plants as energy storage.

In starch crops, most of the six-carbon sugar units are linked together in long, branched chains (called starch). Yeast cannot use these chains to produce ethanol. The starch chains must be broken down into individual six-carbon units or groups of two units. The starch conversion process is relatively simple because the bonds in the starch chain can be broken in an inexpensive manner by the use of heat and enzymes, or by a mild acid solution.

From the standpoint of ethanol production, the long, branched chain arrangement of six-carbon sugar units in starch crops has advantages and disadvantages. The principal disadvantage is the additional equipment, labor, and energy costs associated with breaking down the chain so that the individual sugar units can be used by the yeast.

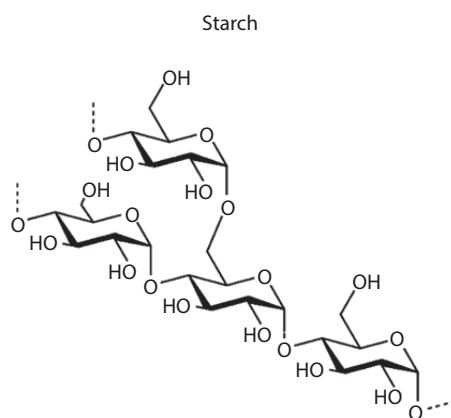
However, this cost is not large in relation to all of the other costs involved in ethanol production. The principal advantage in starch crops is the relative ease with which these crops can be stored, with minimal loss of the fermentable portion. Ease of storage is related to the fact that a conversion step is needed prior to fermentation: many microorganisms, including yeast, can utilize individual or small groups of sugar units, but not long chains. Some microorganisms present in the environment produce the enzymes needed to break up the chains, but unless certain conditions (such as moisture, temperature, and pH) are right, the rate of conversion is slow. When crops and other feeds are dried to approximately 12% moisture – the percentage at which most microorganisms cannot survive – the deterioration of starch and other valuable components (for example, protein and fats) is minimal. There are basically two subcategories of starch crops: grains (e.g., corn, sorghum, wheat, and barley) and tubers (e.g., potatoes and sweet potatoes). The production of beverage-grade ethanol from both types of starch crops is a well-established practice.

Much of the current agronomic research on optimizing the production of ethanol and livestock feed from agricultural crops is focused on unconventional sugar crops such as sweet sorghum. However, opportunities also exist for selecting new varieties of grains and tubers that produce more ethanol per acre. For example, when selecting a wheat variety, protein content is usually emphasized. However, for ethanol production, high starch content is desired. It is well known that wheat varieties with lower protein content and higher starch content usually produce more grain per acre and, consequently, produce more ethanol per acre.

See also: Biomass, Carbohydrates, Sugar Crops.

Starches

Starches are complex carbohydrate polymers (polysaccharides). Starch (*amylum*) is a carbohydrate consisting of a large number of glucose units joined together by glycoside bonds. This polysaccharide is produced by all green plants as a means of storing energy store.



Representation of the Structure of Starch.

Pure starch is a white, tasteless, and odorless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin. Glycogen, the glucose store of animals, is a more branched version of amylopectin.

Starch is processed to produce many of the sugars in processed foods. When dissolved in warm water, starch can be used as a thickening, stiffening, or gluing agent, giving wheat paste.

The starch grains generally provide cheaper ethanol feedstocks, and the conversion is less expensive because they can be stored more easily than most sugar crops, which often must be reduced to a form of syrup prior to the storage. Furthermore, grain distillation produces a by-product that can be used for protein meal in the animal feeds. Fermentation of starch from grains is somewhat more complex than sugars because the starch must first be converted to sugar and then to ethanol.

The simplified equations for the conversion of starch to ethanol can be written as:
Enzymatic hydrolysis of starch to sugars:



Fermentation of sugars to alcohol:



See also: Carbohydrates, Fermentation, Starch Crops.

Steam-Air Gasifier

Most of the gasifiers that are applicable to use as a means of gasifying biomass can be operated on air rather than oxygen if a fuel rather than a synthesis gas is to be produced. In many cases, gasifiers developed specifically for gasification with air are being further developed for relatively pure oxygen feeds.

The gasifier itself is a pressurized fluidized bed system that operates at approximately 1,000°C (1,830°F). In one version of the gasifier, the crushed and dried coal is first devolatilized in a separate fluidized bed reactor. One purpose of the devolatilizing unit is to pretreat caking coals to prevent agglomeration and plugging in the gasifier fluidized bed. Simultaneous removal of sulfur gases by absorption into dolomite has also been tested. Some success has been had in operating the gasifier as a single stage unit without initial coal devolatilization, although bridging problems can arise in this mode. Advantages claimed for the Westinghouse gasifier include the capability of handling all ranks of coals and carbonaceous feedstocks with high carbon conversion, and the absence of tars and oils in the product gas.

Another elevated pressure, fluidized bed gasifier designed originally for steam/air operation is the U-Gas process developed by the Institute of Gas Technology. Operating temperatures are around 1,000°C (1,830°F), the gasifier is a vertical vessel with external cyclones for returning elutriated fines to the bed. A sloped grid at the bottom containing one or more inverted cones serves as the oxidant and steam distributor and an agglomerated ash outlet. Part of the fluidizing steam and oxidant flows through nozzles in the grid, and the remaining gas flows upward at high velocity through a discharge at the cone apex. High temperatures accompany the high velocities, and the ash particles soften and agglomerate, eventually becoming heavy enough to fall out of the bed. The fluidizing velocities are from 0.6 to 1.2 m/s, and the bed is approximately 45% ash. This system is said to produce high carbon conversion efficiencies comparable to slagging gasifiers.

See also: Gasification, Gasifiers.

Steam Explosion

Steam explosion is a pretreatment technology that is applied prior to the hydrolysis of lignocellulosic feedstocks to produce sugars and alcohols.

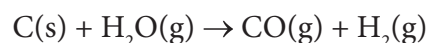
In the process, a lignocellulosic feedstock, such as wood chips, is heated with high-pressure saturated steam [160 to 260°C (320 to 500°F) 100 to 700 psi] for several seconds up to a few minutes. Then, the material is suddenly exposed for atmospheric pressure resulting in an explosive decompression. The process causes hemicellulose degradation and lignin transformation due to high temperature, thus increasing the potential of cellulose hydrolysis. Ninety percent efficiency of enzymatic hydrolysis has been achieved in 24 h for poplar chips, compared to 15% efficiency without pre-treatment.

The factors involved are residence time, temperature, chip size, and moisture content. Optimal solution is obtained by use of high temperature and short residence time (270°C 520°F, 1 minute) or by use of low temperature and long residence time [190°C (375°F), 10 minutes]. Addition of sulfuric acid can effectively improve enzymatic hydrolysis and lead to more complete removal of hemicellulose.

See also: Cellulose, Hydrolysis And Fermentation Of Sugar, Lignin, Wood.

Steam Gasification

Steam gasification reaction is endothermic, i.e., requiring heat input for the reaction to proceed in its forward direction. Usually, an excess amount of steam is also needed to promote the conversion of the carbonaceous feedstock to carbon monoxide and hydrogen:



However, excess steam used in this reaction hurts the thermal efficiency of the process. Therefore, this reaction is typically combined with other gasification reactions in practical applications.

The hydrogen/carbon monoxide ratio of the product synthesis gas depends upon the synthesis chemistry as well as process engineering.

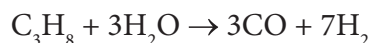
See also: Gasification, Gasifiers.

Steam-Methane Reforming

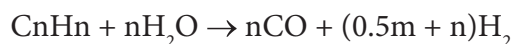
Steam-methane reforming is the benchmark process that has been employed over a period of several decades for hydrogen production. The process involves reforming natural gas in a continuous catalytic process in which the major reaction is the formation of carbon monoxide and hydrogen from methane and steam:



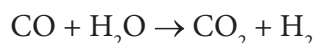
Higher-molecular-weight feedstocks can also be reformed to hydrogen:



That is,

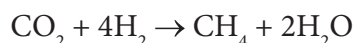
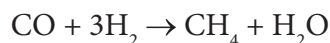


In the actual process, the feedstock is first desulfurized by passage through activated carbon, which may be preceded by caustic and water washes. The desulfurized material is then mixed with steam and passed over a nickel-based catalyst (730 to 845°C, 1,350 to 1,550°F and 400 psi). Effluent gases are cooled by the addition of steam or condensate to approximately 370°C (700°F), at which point carbon monoxide reacts with steam in the presence of iron oxide in a shift converter to produce carbon dioxide and hydrogen:



The carbon dioxide is removed by amine washing; the hydrogen is usually a high-purity (>99%) material.

Since the presence of any carbon monoxide or carbon dioxide in the hydrogen stream can interfere with the chemistry of the catalytic application, a third stage is used to convert of these gases to methane:

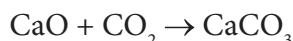


For many refiners, sulfur-free natural gas (CH_4) is not always available to produce hydrogen by this process. In that case, higher-boiling hydrocarbon derivatives (such as propane, butane, or naphtha) may be used as the feedstock to generate hydrogen. The net chemical process for steam methane reforming is then given by the equation:

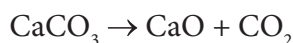


Indirect heating provides the required overall endothermic heat of reaction for the steam-methane reforming.

One way of overcoming the thermodynamic limitation of steam reforming is to remove either hydrogen or carbon dioxide as it is produced, hence shifting the thermodynamic equilibrium towards the product side. The concept for sorption-enhanced methane steam reforming is based on in situ removal of carbon dioxide by a sorbent such as calcium oxide (CaO).



Sorption enhancement enables lower reaction temperatures, which may reduce catalyst coking and sintering, while enabling use of less expensive reactor wall materials. In addition, heat release by the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reactions. However, energy is required to regenerate the sorbent to its oxide form by the energy-intensive calcination reaction, i.e.,



Use of a sorbent requires either that there be parallel reactors operated alternatively and out of phase in reforming and sorbent regeneration modes, or that sorbent be continuously transferred between the reformer/carbonator and regenerator/calciner.

In autothermal (or secondary) reformers, the oxidation of methane supplies the necessary energy and carried out either simultaneously or in advance of the reforming reaction. The equilibrium of the methane steam reaction and the water-gas shift reaction determines the conditions for optimum hydrogen yields. The optimum conditions for hydrogen production require high temperature at the exit of the reforming reactor (800 to 900°C; 1,470 to 1,650°F), high excess of steam (molar steam-to-carbon ratio of 2.5 to 3), and relatively low pressures (below 450 psi). Most commercial plants employ supported nickel catalysts for the process.

The steam-methane reforming process described briefly above would be an ideal hydrogen production process if it was not for the fact that large quantities of natural gas, a valuable resource, are required as both feed gas and combustion fuel. For each mole of methane reformed, more than one mole of carbon dioxide is co-produced and must be disposed. This can be a major issue as it results in the same amount of greenhouse gas emission as would be expected from direct combustion of natural gas or methane. In fact, the production of hydrogen as a clean burning fuel by way of steam reforming of methane and other fossil-based hydrocarbon fuels is not in environmental balance if in the process, carbon dioxide and carbon monoxide are generated and released into the atmosphere, although alternate scenarios are available. Moreover, as the reforming process is not totally efficient, some of the energy value of the hydrocarbon fuel is lost by conversion to hydrogen but with no tangible environmental benefit, such as a reduction in emission of greenhouse gases. Despite these apparent shortcomings, the process has the following advantages: (i) produces 4 moles of hydrogen for each mole of methane consumed, (ii) feedstocks for the process (methane and water are readily available), (iii) the process is adaptable to a wide range of hydrocarbon feedstocks, (iv) operates at low pressures, less than 450 psi, (v) requires a low steam/carbon ratio on the order of 2.5 to 3, (vi) good utilization of input energy (reaching 93%), (vii) can use catalysts that are stable and resist poisoning, and (viii) good process kinetics.

Liquid feedstocks, either liquefied petroleum gas or naphtha, can also provide backup feed, if there is a risk of natural gas curtailments. The feed handling system needs to include a surge drum, feed pump, vaporizer (usually steam-heated) followed by further heating before desulfurization. The sulfur in liquid feedstocks occurs as mercaptans, thiophene derivatives, or higher-boiling compounds. These compounds are stable and will not be removed by zinc oxide; therefore, a hydrogenation unit will be required. In addition, as with refinery gas, olefins must also be hydrogenated if they are present.

The reformer will generally use a potash-promoted catalyst to avoid coke buildup from cracking of the higher-boiling feedstock. If liquefied petroleum gas is to be used only occasionally, it is often possible to use a methane-type catalyst at a higher steam/carbon ratio to avoid coking. Naphtha will require a promoted catalyst unless a pre-former is used.

Steam-Naphtha Reforming

Steam-naphtha reforming is a continuous process for the production of hydrogen from liquid hydrocarbon derivatives and is, in fact, similar to steam-methane reforming that is one of several possible processes for the production of hydrogen from low-boiling hydrocarbon derivatives other than ethane. A variety of naphtha-types in the naphtha boiling range may be employed, including feeds containing up to 35% aromatics. Thus, following pretreatment to remove sulfur compounds, the feedstock is mixed with steam and taken to the reforming furnace (675 to 815°C, 1,250 to 1,500°F, 300 psi, 2,068 kPa), where hydrogen is produced.

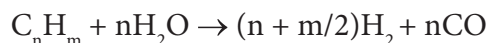
Steam Reforming

Steam reforming (sometimes referred to as reforming or steam methane reforming) is another well-known method for making hydrogen. Natural gas is the most common fuel used in steam reforming.

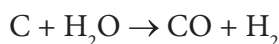
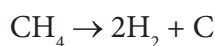
In the steam reforming process, low-boiling hydrocarbon derivatives such as methane are reacted with steam to form hydrogen:



H is the heat of reaction. A more general form of the equation that shows the chemical balance for higher-boiling hydrocarbon derivatives is:



The reaction is typically carried out at approximately 815°C (1,500°F) over a nickel catalyst packed into the tubes of a reforming furnace. The high temperature also causes the hydrocarbon feedstock to undergo a series of cracking reactions, plus the reaction of carbon with steam:



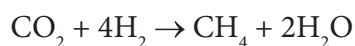
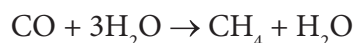
Carbon is produced on the catalyst at the same time that hydrocarbon is reformed to hydrogen and carbon monoxide. With natural gas or similar feedstock, reforming predominates and the carbon can be removed by reaction with steam as fast as it is formed. When higher-boiling feedstocks are used, the carbon is not removed fast enough and builds up, thereby requiring catalyst regeneration or replacement. Carbon buildup on the catalyst (when high-boiling feedstocks are employed) can be avoided by the addition of alkali compounds, such as potash, to the catalyst, thereby encouraging or promoting the carbon-steam reaction.

However, even with an alkali-promoted catalyst, feedstock cracking limits the process to hydrocarbon derivatives with a boiling point less than 180°C (350°F). Natural gas, propane, butane, and low-boiling naphtha are most suitable. Pre-reforming, a process that uses an adiabatic catalyst bed operating at a lower temperature, can be used as a pretreatment to allow higher-boiling feedstocks to be used with lower potential for carbon deposition (coke formation) on the catalyst.

After reforming, the carbon monoxide in the gas is reacted with steam to form additional hydrogen (the water-gas shift reaction):



This leaves a mixture consisting primarily of hydrogen and carbon monoxide that is removed by conversion to methane:



The critical variables for steam reforming processes are (i) temperature, (ii) pressure, and (iii) the steam/hydrocarbon ratio. Steam reforming is an equilibrium reaction, and conversion of the hydrocarbon feedstock is favored by high temperature, which in turn requires higher fuel use. Because of the volume increase in the reaction, conversion is also favored by low pressure, which conflicts with the need to supply the hydrogen at high pressure. In practice, materials of construction limit temperature and pressure.

On the other hand, and in contrast to reforming, shift conversion is favored by low temperature. The gas from the reformer is reacted over iron oxide catalyst at 315 to 370°C (600 to 700°F) with the lower limit being dictated activity of the catalyst at low temperature.

Hydrogen can also be produced by partial oxidation (POX) of hydrocarbon derivatives in which the hydrocarbon is oxidized in a limited or controlled supply of oxygen:



The shift reaction also occurs, and a mixture of carbon monoxide and carbon dioxide is produced in addition to hydrogen. The catalyst tube materials do not limit the reaction temperatures in partial oxidation processes, and higher temperatures may be used that enhance the conversion of methane to hydrogen. Indeed, much of the design and operation of hydrogen plants involves protecting the reforming catalyst and the catalyst tubes because of the extreme temperatures and the sensitivity of the catalyst. In fact, minor variations in feedstock composition or operating conditions can have significant effects on the life of the catalyst or the reformer itself. This is particularly true of changes in molecular weight of the feed gas, or poor distribution of heat to the catalyst tubes.

Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the lower-boiling feedstocks that are required for steam reforming. Partial oxidation processes were first considered for hydrogen production because of expected shortages of lower-boiling feedstocks and the need to have available a disposal method for higher-boiling, high-sulfur streams such as asphalt or crude oil coke.

Catalytic partial oxidation, also known as auto-thermal reforming, reacts oxygen with a low-boiling feedstock and by passing the resulting hot mixture over a reforming catalyst. The use of a catalyst allows the use of lower temperatures than in non-catalytic partial oxidation and which causes a reduction in oxygen demand.

The feedstock requirements for catalytic partial oxidation processes are similar to the feedstock requirements for steam reforming, and low-boiling hydrocarbon derivatives from refinery gas to naphtha are preferred. The oxygen substitutes for much of the steam in preventing coking and a lower steam/carbon ratio is required. In addition, because a large excess of steam is not required, catalytic partial oxidation produces more carbon monoxide and less hydrogen than steam reforming.

The steam reforming process is the most common method used to make hydrogen industrially. One benefit is that it is cheaper than producing hydrogen by electrolysis. However, a big drawback is the amount of carbon dioxide produced during the process. If the steam reforming process is to catch on as a means of mass-producing hydrogen fuel, the issue of what to do with the carbon dioxide produced must be addressed. Carbon dioxide can build up and trap heat on the planet. This condition is known as global warming. Potential solutions to the carbon dioxide issue with steam reforming exist, and all are costly. The carbon dioxide could be stored in empty gas wells or oil wells where the reservoirs of gas or oil have been depleted. Saline aquifers, which are underground pockets of saltwater, are another storage possibility. So are coal seams (where coal can be found) that are so deep underground that they cannot be mined.

Another positive aspect is that of all the fossil fuels, natural gas is the cleanest burning. In other words, it gives off fewer by-products that can contribute to pollution. The use of natural gas to make hydrogen might help in the creation of an infrastructure for the distribution of hydrogen. Since there are stations that already distribute natural gas, the natural gas could be transported there and converted to hydrogen via steam reforming on site and on a small scale. This means of production could provide hydrogen for cars that run on either hydrogen fuel cells or hydrogen-powered internal combustion engines.

Steam Regenerative Caustic Treating Process

The gas processing (gas cleaning, gas treating) industry. The hydrocarbon processing industry has historically used caustic solutions to extract or treat acidic impurities (mainly RSH) in hydrocarbon liquid streams. When quantities of

acid gas contaminants are small (typically less than 200 ppm w/w), a simple caustic wash is effective and economical. However, as the quantity of acid gas contaminants rises, once-through caustic washing processes can be expensive due to high chemical consumption and disposal costs of nonregenerable byproducts, making this approach impractical.

Several caustic processes, both regenerative and non-regenerative, can be used to remove sulfur compounds from gas streams. The method or combination of methods that can be used depends on the mercaptan characteristics and the product specification that must be met.

One of the common processes for treating hydrocarbon liquids is the use of regenerative caustic wash with sodium hydroxide (NaOH). The high pH allows the caustic to react with the weakly acidic mercaptan derivatives to form mercaptide salts followed by conversion of the mercaptides to disulfides by oxidation. These disulfides will remain in the sweetened hydrocarbon product, and the overall sulfur content of the gas stream remains unchanged. However, the sulfur leaves as odorless disulfide derivatives rather than mercaptans that are quite malodorous even at ppm levels.

The steam-regenerative caustic treating process is directed toward removal of mercaptans from such products as low-boiling, straight-run naphtha. The caustic is regenerated by steam blowing in a stripping tower. The nature and concentration of the mercaptans to be removed dictate the quantity and temperature of the process. However, the caustic solution gradually deteriorates because of the accumulation of material that cannot be removed by stripping; the caustic quality must be maintained by either continuous or intermittent discard, and replacement, of a minimum amount of the operating solution.

Non-regenerative caustic treatment processes are applicable if the concentrations of the contaminants are low. The use of a non-regenerative solid potassium hydroxide (KOH) bed is effective for removal of hydrogen sulfide but not for other sulfur compounds. However, this type of treatment process produces a waste spent caustic stream that must be further processed and disposed. Since the caustic is consumed and requires continuous makeup, there is an associated operating cost.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Steam Turbine

The steam turbine is a device that extracts thermal energy from pressurized steam and uses it to do mechanical work on a rotating output shaft. The turbine is a form of heat engine that derives much of its improvement in thermodynamic efficiency from the use of multiple stages in the expansion of the steam, which results in a closer approach to the ideal reversible expansion process. Because the turbine generates rotary motion, it is particularly suited to be used to drive an electrical generator (Figure S-3).

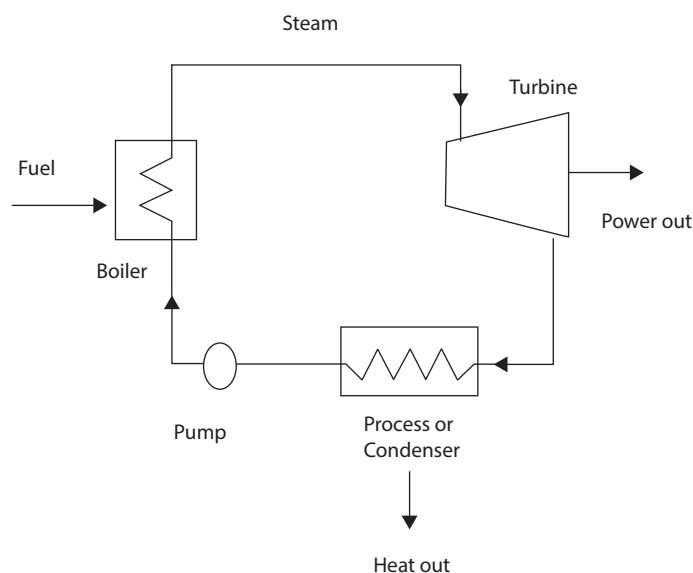


Figure S-3 A steam turbine generator system.

The turbine blades are of two basic types: (i) blades and (ii) nozzles (Figure S-4). Blades move entirely due to the impact of steam on them, and their profiles do not converge. This results in a steam velocity drop and essentially no pressure drop as steam moves through the blades. A turbine composed of blades alternating with fixed nozzles is referred to as an impulse turbine – other names such as Curtis turbine, Rateau turbine, and Brown-Curtis turbine are also used.

Nozzles appear similar to blades, but their profiles converge near the exit. This results in a steam pressure drop and velocity increase as steam moves through the nozzles. Nozzles move due to both the impact of steam on them and the reaction due to the high-velocity steam at the exit. A turbine composed of moving nozzles alternating with fixed nozzles is often referred to as a reaction turbine or a Parsons turbine.

Horizontal axis	Cross-flow axis	Vertical axis
Straight axis		SC-Darrieus
Solid mooring		(straight blade)
Buoyant mooring		H-Darrieus
Buoyant mooring		(straight blade)
		Darrieus
		(curved blade)
		Gorlov
		(helical blade)
		Savonius
		(straight/curved blade)

Figure S-4 Types of turbine blades.

Except for low-power applications, turbine blades are arranged in multiple stages (compounding) which greatly improves efficiency at low speeds. A reaction stage is a row of fixed nozzles followed by a row of moving nozzles. Multiple reaction stages divide the pressure drop between the steam inlet and exhaust into numerous small drops, resulting in a pressure-compounded turbine. Impulse stages may be pressure-compounded, velocity-compounded, or pressure-velocity compounded. A pressure-compounded impulse stage is a row of fixed nozzles followed by a row of moving blades, with multiple stages for compounding. This is also known as a Rateau turbine, after its inventor. A velocity-compounded impulse stage (also called a Curtis wheel) is a row of fixed nozzles followed by two or more rows of moving blades alternating with rows of fixed blades. This divides the velocity drop across the stage into several smaller drops. A series of velocity-compounded impulse stages is referred to as a pressure-velocity compounded turbine.

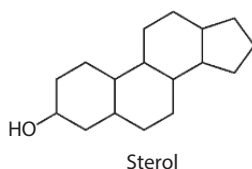
Steam turbines differ from reciprocating engines, internal combustion engines, and gas turbines in that the fuel is burned in a piece of equipment, the boiler, which is separate from the power generation equipment. The energy is transferred from the boiler to the steam turbine generator by an intermediate medium, typically steam under pressure. As mentioned previously, this separation of functions enables steam turbines to operate with an enormous variety of fuels. The topic of boiler fuels, their handling, combustion, and the clean-up of the effluents of such combustion is a separate and complex issue that is addressed in the fuels and emissions sections of this report.

For sizes up to (approximately) 40 MW, horizontal industrial boilers are built. This enables them to be shipped via rail car, with considerable cost savings and improved quality, as the cost and quality of factory labor is usually both lower in cost and greater in quality than field labor. Large shop-assembled boilers are typically capable of firing only gas or distillate oil, as there is inadequate residence time for complete combustion of most solid and residual fuels in such designs. Large, field-erected industrial boilers firing solid and residual fuels bear a resemblance to utility boilers except for the actual solid fuel injection. Large boilers usually burn pulverized coal; however, intermediate and small boilers burning coal or solid fuel employ various types of solids feeders.

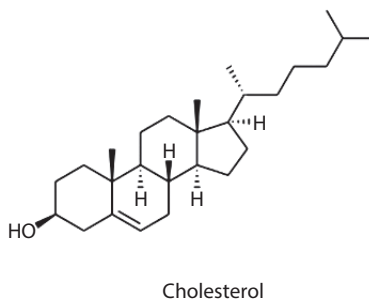
See also: Electricity Generation – Equipment, Rankine Cycle, Turbine.

Sterols

Sterol is a chemical compound with the formula $C_{17}H_{28}O$. The name is also used generically for compounds that are derived from this one by substituting other chemical groups for some of the hydrogen atoms, or modifying the bonds in the ring.



The sterols (or steroid alcohols) are a subgroup of the steroids and an important class of organic molecule which occur naturally in plants, animals, and fungi. The most familiar type of animal sterol is cholesterol which is vital to cell membrane structure, and functions as a precursor to fat-soluble vitamins and steroid hormones.



Sterols, which are based on a saturated, condensed ring structure, are widely distributed in animals and plants and are also believed to be source material for crude oil, although little is known of their natural degradation reactions. Additional classes of compounds that also make up the source material are lipids and terpenoids and, possibly, the humic substances, specifically humic acids and, to a lesser extent, fulvic acids.

Stoker Combustors

Stoker combustors improve on operation of the pile burners by providing a moving grate which permits continuous ash collection, thus eliminating the cyclic operation characteristic of traditional pile burners. In addition, the fuel is spread more evenly, normally by a pneumatic stoker, and in a thinner layer in the combustion zone, giving more efficient combustion.

Stoker-fired boilers were first introduced in the 1920s for coal, and in the late 1940s, the Detroit Stoker Company installed the first traveling grate spreader stoker boiler for wood. In the basic stoker design, the bottom of the furnace is a moving grate which is cooled by under-fire air. The under-fire air rate defines the maximum temperature of the grate and thus the allowable feed moisture content. More modern designs include the Kablitz grate, a sloping reciprocating water-cooled grate. Reciprocating grates are attractive because of simplicity and low fly ash carry-over. Combustion is completed by the use of overfire air. The furnace wall configurations include straight and bull nose water walls.

See also: Combustion.

Straight Vegetable Oil

In common use, the term vegetable oil may refer exclusively to vegetable fats which are liquid at room temperature. Also, straight-run vegetable oil is vegetable oil that has been distilled and not used for any other purpose. Once used for, say cooking, the vegetable oil may be referred to as used cooking oil or waste cooking oil and is not suitable for use as a vehicle fuel because of the potential contaminant that could interfere with the smooth running of the engine.

Vegetable oils are usually edible; non-edible oils derived mainly from petroleum are termed mineral oils. Vegetable oil is extracted from seeds, or less often, from other parts of fruits and are mixtures of triglyceride derivatives. Soybean

oil, grape seed oil, and cocoa butter are examples of fats from seeds. Olive oil and palm oil are examples of oils. Straight-run vegetable oil is any vegetable oil that has not been optimized through the process of transesterification.

Vegetable oil can power a diesel-engine vehicle, but the effects on the environment are still unclear and debatable. Often referred to as veggie cars or grease cars, these vehicles have fuel systems modified to burn both diesel fuel and straight vegetable oil.

See also: Biomass, Vegetable Oil.

Stratosphere

The stratosphere forms the middle layer of the homosphere and lies directly above the troposphere in which the temperature rises to a maximum of ca. -2°C (28°F) with increasing altitude. This phenomenon is due to the presence of ozone (O_3) which may reach a level of around 10 ppm v/v in the mid-range of the stratosphere. The heating effect is caused by the absorption of ultraviolet radiation energy by ozone. The situation can become even more complicated due to the formation of additional ozone in the gaseous plumes from urban centers.

The stratosphere has a thickness in excess of 25 miles thick and contains the infamous ozone layer. Temperature increases upward in the stratosphere as ozone molecules concentrated in the upper two-thirds of the layer absorb ultraviolet solar radiation, and decreasing air density results in greater agitation (more kinetic energy) of atoms. Maximum temperatures approach 0°C (32°F) at the stratopause that separates the stratosphere and the overlying mesosphere. The warm cap of the stratosphere overlying the relatively cool troposphere results in a stable atmospheric configuration as the cool air cannot rise into the warm layer.

Straw

Straw (residual herbaceous biomass) is the main residual herbaceous material for energy application nowadays.

As it is a residual product, its availability for energy purposes is driven by the cereals markets and does not have autonomous market behavior. In addition, farms consume significant quantities of straw internally – as bed material for livestock, grain drying, etc. Some straw is also chaffed and returned back to the field as soil ameliorator. The net straw yield per hectare for energy application also depends on the crop, the grain yield per hectare, climate and cultivation conditions, etc. Nevertheless, one can roughly estimate that the average straw yield per hectare is approximately 50 to 65% of the grain yield per hectare from cereals and oilseeds.

Similar to herbaceous crops, straw usually has lower moisture content than woody biomass. Conversely, it has a lower calorific value, bulk density, ash melting point and higher content of ash, and problematic inorganic component such as chlorine, potassium, and sulfur, which cause corrosion and pollution. The last two drawbacks can be relatively easily overcome by leaving straw on the field for a while. In such a way, rainfall “washes” it naturally from a large part of potassium and chlorine. Alternatively, fresh straw can be directly shipped to the gasification plant, where it is washed by dedicated facilities at moderate temperatures (50 to 60°C ; 120 to 140°F). Due to washing, the initially low moisture content of straw becomes higher in both cases, and hence, a mandatory drying is applied afterwards. In both cases also, the content of corrosive components is reduced, but not completely taken out.

In order to decrease handling costs, straw and dedicated herbaceous energy crops are usually baled before being shipped to the gasification plant. The weight and the size of bales depend on the baling equipment and on the requirements of the gasification plant.

See also: Crop Residues.

Stretford Process

The Stretford process is one of the oldest commercial liquid redox processes, and it is based on a vanadium and anthraquinone redox system. The process was developed to remove hydrogen sulfide (H_2S) from town gas and was the first liquid phase, oxidation process for converting hydrogen sulfide into sulfur to gain widespread commercial

acceptance. The process is a wet oxidation process and employs a solution containing vanadium salts and anthraquinone disulfonic acid. Most hydrogen sulfide removal processes return the hydrogen sulfide unchanged, but if the quantity involved does not justify installation of a sulfur recovery plant (usually a Claus plant), it is necessary to select a process that directly produces elemental sulfur.

The Stretford Process removes hydrogen sulfide by continuous liquid washing using an adequate alkaline solution containing dyestuff intermediates. The hydrogen sulfide is converted to elemental sulfur, which is separated from the solution, washed to remove the solution from the sulfur cake, and stored ready for disposal. The process was the first liquid phase, oxidation process for converting hydrogen sulfide into sulfur to gain widespread commercial acceptance. The process uses reduction-oxidation (redox) chemistry to oxidize the hydrogen sulfide into elemental sulfur, in an alkaline solution containing vanadium as an oxygen carrier.

See also: Gas Cleaning, Gas Processing, Gas Treating, Redox Processes.

Stripping

Stripping is a physical separation process in which one or more components are removed from a liquid stream by a vapor stream. In industrial applications, the liquid and vapor streams can have co-current or countercurrent flows. Stripping is usually carried out in either a packed or trayed column and works on the basis of mass transfer in which the component in the liquid phase is transferred to the vapor phase. Stripping is mainly conducted in trayed towers (plate columns) and packed columns, and less often in bubble columns, spray towers, and centrifugal contactors.

Trayed towers consist of a vertical column with liquid flowing in the top and out the bottom. The vapor phase enters in the bottom of the column and exits out of the top. Inside of the column are trays or plates. These trays force the liquid to flow back and forth horizontally, while the vapor bubbles up through holes in the trays. The purpose of these trays is to increase the amount of contact area between the liquid and vapor phases.

Packed columns are similar to trayed columns in that the liquid and vapor flows enter and exit in the same manner. The difference is that in packed towers, there are no trays. Instead, packing is used to increase the contact area between the liquid and vapor phases. There are many different types of packing used, and each one has advantages and disadvantages.

Frequently, air, steam, and inert gases (including hydrocarbon gases) and is based on solubility, stability, corrosivity, and availability. As stripping agents are gases, operation at nearly the highest temperature and lowest pressure that will maintain the components and not vaporize the liquid feed stream is desired. This allows for the minimization of flow. As with all other variables, minimizing cost while achieving efficient separation is the ultimate goal.

The size of the equipment, and particularly the height and diameter, is important in determining the possibility of flow channeling that would reduce the contact area between the liquid and vapor streams. If flow channeling is suspected to be occurring, a redistribution plate is often necessary to, as the name indicates, redistribute the liquid flow evenly to reestablish a higher contact area.

Packed columns, and particularly when random packing is used, are usually favored for smaller columns with a diameter less than 2 feet and a packed height of not more than 20 feet. Packed columns can also be advantageous for corrosive fluids, high foaming fluids, when fluid velocity is high, and when particularly low pressure drop is desired. Trayed strippers are advantageous because of ease of design and scale up. Structured packing can be used similar to trays despite possibly being the same material as dumped (random) packing. Using structured packing is a common method to increase the capacity for separation or to replace damaged trays.

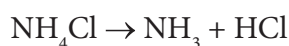
Trayed strippers can have sieve, valve, or bubble cap trays, while packed strippers can have either structured packing or random packing. Trays and packing are used to increase the contact area over which mass transfer can occur as mass transfer theory dictates. Packing can have varying material, surface area, flow area, and associated pressure drop. Older generation packing includes ceramic Raschig rings and Berl saddles. More common packing materials are metal and plastic Pall rings, metal and plastic Bialecki rings, and ceramic Intralox saddles. Each packing material of this newer generation improves the surface area, the flow area, and/or the associated pressure drop across the packing. Also important is the ability of the packing material to not stack on top of itself. If such stacking occurs, it drastically reduces the surface area of the material. Lattice design work has been increasing of late that will further improve these characteristics.

During operation, monitoring the pressure drop across the column can help to determine the performance of the stripper. A changed pressure drop over a significant range of time can be an indication that the packing may need to be replaced or cleaned.

See also: Gas Cleaning, Gas Processing, Gas Treating, Scrubbing.

Sublimation

The term *sublimation* refers to a *physical* change of state and is not used to describe the transformation of a solid to a gas in a chemical reaction. In the process, a substance undergoes a transition directly from the solid phase to the gas phase without passing through the intermediate liquid phase (Table 7.4). For example, the dissociation on heating of solid ammonium chloride (NH_4Cl) into ammonia (NH_3) and hydrogen chloride (HCl) is *not* sublimation but a chemical reaction:



Sublimation requires additional energy and is an endothermic change, and the enthalpy of sublimation (also referred to as the *heat of sublimation*) can be calculated by adding the enthalpy of fusion and the enthalpy of vaporization. The reverse process of sublimation is the process of *deposition* in which some chemicals pass directly from the gas phase to the solid phase, again without passing through the intermediate liquid phase.

Sublimation:

Solid $\rightarrow$ gas

Deposition

Gas $\rightarrow$ solid

See also: Deposition, Evaporation.

Sugar Beets

Sugar beets and fodder beets were found to be not adapted for growth in the Southeast. While early growth was satisfactory, foliage diseases caused severe defoliation in late July and August. Regrowth of leaves was made at the expense of stored sugars; thus, yield and sugar concentrations in the roots at harvest were only approximately half of what is observed in the major beet growing areas.

Sugar beet (*Beta vulgaris*, family-Chenopodiaceae) is yet another plant which contains a high percentage of sugars stored in fleshy storage roots. It is also an important source for production of sugar as well as ethanol.

Raising crops like sugarcane, sugar beet, tapioca, potato, maize, etc., purely for production of ethanol is described as energy cropping, and the crops are called energy crops. Cultivation of plants (trees) for obtaining fuel/fire wood is described as energy plantation.

Other plants, such as Euphorbiaceae plants like *Euphorbia lathyris*, milkweed (*Asclepia speciosa*) and the tree legume *Copaifera multijuga*, produce hydrocarbon derivatives which can be converted into and used as diesel, called biodiesel. In addition, some freshwater and marine algae are also known to accumulate hydrocarbon derivatives. Some algae like Chlamydomonas and anaerobic bacteria like Clostridium produce hydrogen gas, which can be used as a pollution-free fuel. Long-term research efforts are needed to develop these organisms as sources of bioenergy.

The euphorbeans and milkweeds can be grown in relatively dry environments on lands not suited for crop production; this makes them highly attractive sources of biofuels. The Euphorbias are relatives of plants used to produce rubber; they produce a latex, which has approximately 30% hydrocarbon derivatives emulsified in water.

However, hydrocarbon derivatives, as such, are not usually produced from crops, there being insufficient amount of the hydrocarbon derivatives present in the plant tissue to make the process economical. However, biodiesel is produced from crops, thereby offering an excellent renewable fuel for diesel engines.

See also: Sugar Crops, Starch, Sugars.

Sugar Cane

Sugarcane (sugar cane, *Saccharum officinarum* - family Gramineae) is the main source of raw material for sugar industry. The wastes from sugar industry include bagasse, molasses, and press mud. After extracting the cane juice for sugar production, the cellulosic fibrous residue that remains is called bagasse. It is used as the raw material (biomass) and processed variously for the production of fuel, alcohols, single cell protein as well as in paper mills. Molasses is an important by-product of sugar mills and contains 50-55% fermentable sugars. One ton of molasses can produce approximately 280 liters of ethanol. Molasses is used for the production of animal feed, liquid fuel, and alcoholic beverages.

Sugarcane residues, particularly sugarcane bagasse (SB) and leaves (SL), have been explored for both biotechnological and non-biotechnological applications. For the last three decades, sugarcane bagasse and leaves have been explored for use in lignocellulosic bioconversion, which offers opportunities for the economic utilization of residual substrates in the production of bioethanol and value-added commercial products such as xylitol, specialty enzymes, organic acids, and single-cell protein. In addition, sugarcane was the basis for the first renewable biofuel program in Brazil. Corn is the basis for the present renewable ethanol fuel industry in the United States.

Also, sugar beet, corn, and sweet sorghum are agricultural crops presently grown commercially for both carbohydrate production and animal feeds. Sugarcane, corn, and sweet sorghum are efficient at trapping solar energy and use specific biochemical pathways to recycle and trap carbon dioxide that is lost through photorespiration. Sugar beets are efficient because they store their carbohydrate in the ground.

The sugars produced by these crops are easily fermented by *Saccharomyces cerevisiae*. The sucrose produced by sugarcane, sugar beet, and sweet sorghum can be fermented directly after squeezing them from the crop. Corn traps its carbohydrate largely in the form of starch which must first be converted into glucose through saccharification with glucoamylase. The residues left over after removing fermentable sugars can also be utilized. In some cases, they end up as animal feeds, but many agricultural residues can be converted into additional fermentable sugars through saccharification with cellulase and hemicellulase. The hemicellulose sugars are not fermentable by *S. cerevisiae*, and must be converted to ethanol by pentose fermenting yeasts or genetically engineered organisms.

See also: Sugar Crops, Starch, Sugars.

Sugar Crops

Interest in ethanol production from agricultural crops has prompted research on the development of sugar crops that have not been cultivated on a widespread commercial basis in this country. Three of the principal crops now under investigation are sweet sorghum, Jerusalem artichokes, and fodder beets.

Preparation is basically a crushing and extraction of the sugars which the yeast can immediately use. But sugar crops must be dealt with fairly quickly before their high sugar and water content. The characteristics of sugar crops are variable (Table S-3), but, in general, because of the danger of such spoilage, the storage of sugar crops is not always practical.

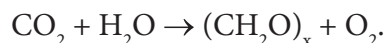
Table S-3 Characteristics of sugar crops.

Crop	Description
Sugar Cane	High yields per acre of both sugar and crop residue are strong points of sugar cane production. The crop residue, called bagasse, is used in Brazil to provide heat for the distilleries.
Sugar beet	Although sugar beets are grown in many areas of the U.S., they must be rotated with non-root crops (1 beet crop per 4-year period is the general rule). While beet by-products cannot provide fuel for the distillery, the beet pulp and tops are excellent feed in wet or dry form. Or the tops may be left on the field for fertilizer and erosion control.
Sweet Sorghum	Sweet sorghum is a name given to varieties of a species of sorghum: <i>Sorghum bicolor</i> . This crop has been cultivated on a small scale in the past for production of table syrup, but other varieties can be grown for production of sugar. The most common types of sorghum species are those used for production of grain.
Jerusalem Artichoke	The Jerusalem artichoke has shown excellent potential as an alternative sugar crop. A member of the sunflower family, this crop is native to North America and well-adapted to northern climates. Like the sugar beet, the Jerusalem artichoke produces sugar in the top growth and stores it in the roots and tuber. It can grow in a variety of soils, and it is not demanding of soil fertility. The Jerusalem artichoke is a perennial; small tubers left in the field will produce the next crop for the next season, so no plowing or seeding is necessary.
Fodder Beets	Another promising sugar crop which presently is being developed in New Zealand is the fodder beet. The fodder beet is a high-yielding forage crop obtained by crossing two other beet species, sugar beets and mangolds. It is similar in most agronomic respects to sugar beets. The attraction of this crop lies in its higher yield of fermentable sugars per acre relative to sugar beets and its comparatively high resistance to loss of fermentable sugars during storage.
Fruit Crops	Fruit crops (e.g., grapes, apricots, peaches, and pears) are another type of feedstock in the sugar crop category. Typically, fruit crops such as grapes are used as the feedstock in wine production. These crops are not likely to be used as feedstocks for production of fuel-grade ethanol because of their high market value for direct human consumption. However, the co-products of processing fruit crops are likely to be used as feedstocks because fermentation is an economical method for reducing the potential environmental impact of untreated wastes containing fermentable sugars.

See also: Starch Crops.

Sugars and Starch

Biomass is typically composed of 75 to 90% by weight sugar species, the other 10 to 25 wt% being mainly lignin. Plants capture solar energy as fixed carbon during which carbon dioxide is converted to water and sugars $(\text{CH}_2\text{O})_x$:



The sugars produced are stored in three types of polymeric macromolecules: (i) starch, (ii) cellulose, and (iii) hemicellulose. Monosaccharides (the simple sugars) are colorless, water-soluble crystalline solids with a characteristic three-dimensional structure (Figure S-5).

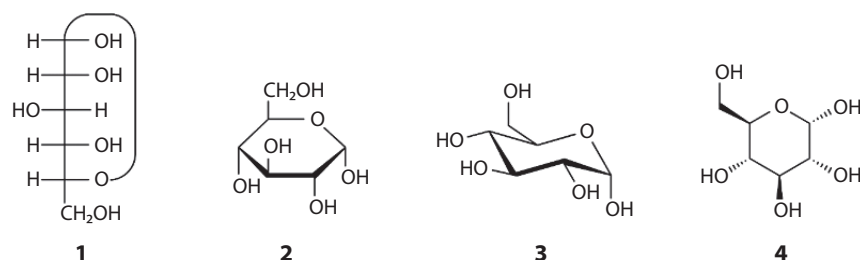


Figure S-5 Representations of the naturally occurring form of glucose.

Because of the presence of numerous chiral centers (place in the molecule in which one atom is bonded to four different chemical species), various isomeric forms of the different monosaccharides exist. However, since biofuels are necessarily obtained from natural sources, the forms which are abundant in nature predominate.

In general, sugar polymers such as cellulose and starch (Figure S-6) can be readily broken down to their constituent monomers by hydrolysis, preparatory to conversion to ethanol or other chemicals. In contrast, lignin is a complex structure containing aromatic groups and is less readily degraded.

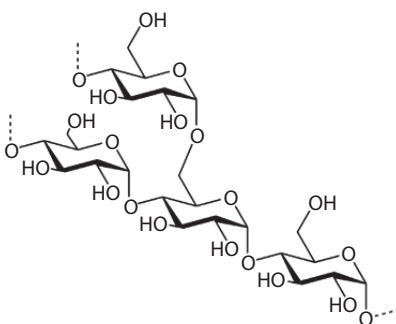
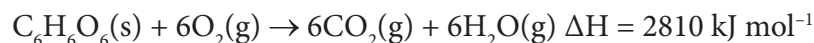


Figure S-6 Representation of the starch molecule.

Although lignocellulose is one of the cheapest and most abundant forms of biomass, it is difficult to convert this relatively unreactive material into sugars. Among other factors, the walls of lignocellulose are composed of lignin, which must be broken down in order to render the cellulose and hemicellulose accessible to acid hydrolysis. For this reason, many programs focused on ethanol production from biomass are based almost entirely on the fermentation of sugars derived from the starch in corn grain, which has increased in production over the past century (Figure 4).

Glucose (dextrose), fructose (laevulose), galactose, xylose, and ribose are common. Glucose is a simple sugar that can be readily fermented into biofuel if it can be accessed; the equation for its combustion is given here:



A large amount of heat energy is evolved in the complete combustion of one mole of pure glucose, and this exothermic reaction is the main source of metabolic energy (ATP) in cells. Glucose and other simple sugars are normally fermented into alcohols for direct use as a fuel. Starch, otherwise known as amyllum, is the polysaccharide present in all green plants and is the form by which food is stored. Glucose monomers are joined by β 1-4 glycosidic bonds in the linear helical portions of the polymer (amylose) and by β 1-5 glycosidic bonds in the branched portions (amylopectin). Plant sugars or starches of biofuel crops such as sugar cane and maize are fermented to produce ethanol.

The most widely used form of sugar for ethanol fermentation is the blackstrap molasses which contains approximately 30 to 40% w/w sucrose, 15 to 20% w/w invert sugars such as glucose and fructose, and 28 to 35% w/w of non-sugar solids.

The direct fermentation of sugarcane juice, sugar beet juice, beet molasses, fresh and dried fruits, sorghum, whey, and skim milk has been considered, but none of these could compete economically with molasses. From the viewpoint of industrial ethanol production, sucrose-based substances such as sugarcane and sugar beet juices present

many advantages including their relative abundance and renewable nature. Molasses, the non-crystallizable residue that remains after the sucrose purification, has additional advantages; it is relatively inexpensive raw material, readily available, and already used for industrial ethanol production.

See also: Carbohydrates, Sugar Crops.

Sulfa-Check Process

The Sulfa-Check process selectively removes hydrogen sulfide and mercaptans from natural gas in the presence of carbon dioxide. The process uses sodium nitrite (NaNO_2).

Gas streams with elevated oxygen levels with the Sulfa-Check process will produce some nitrogen oxides in the gas stream. Removal of hydrogen sulfide is not affected under short contact times, as the reaction is almost instantaneous. Sodium hydroxide and sodium nitrite are consumables in the processes and cannot be regenerated.

This process is accomplished in a one-step single vessel design using an aqueous solution of sodium nitrite buffered to stabilize the pH above 8. Also, there is enough strong base to raise the pH of the fresh material to 12.5. The claimed reaction with hydrogen sulfide forms elemental sulfur, ammonia, and caustic soda as follows:



Other reactions forming the oxides of nitrogen do occur, and carbon dioxide in the gas reacts with the sodium hydroxide to form sodium carbonate and sodium bicarbonate. The spent solution is a slurry of fine sulfur particles in a solution of sodium and ammonium salts.

Gas streams with elevated oxygen levels will produce some nitrogen oxides in the gas stream, and carbon dioxide in the gas reacts with sodium hydroxide to form sodium carbonate and sodium bicarbonate. Removal of hydrogen sulfide is not affected under short contact times since the reaction is almost instantaneous. Sodium hydroxide and sodium nitrite are consumables in the processes and cannot be regenerated.

See also: Gas Cleaning, Gas Processing, Gas Treating.

SulfaClean HC Liquid Sweetening Process

The SulfaClean Process uses SulfaClean HC, a granular material that is used to remove aggregative sulfur compounds, primarily hydrogen sulfide (H_2S), in a variety of clear liquid streams.

Propane/propylene, butane, liquefied natural gas, natural gas liquids, naphtha, and other low-molecular-weight liquid hydrocarbon streams treatment reduces corrosion to pass copper strip testing and meet hydrogen sulfide limits. Dry or water saturated liquid hydrocarbon derivatives can be treated, as well as water or brines for removal of dissolved hydrogen sulfide prior to disposal.

In the process, liquids flow upward through the SulfaClean HC media. Flow rates and the system design depend on fluid type and contaminants' quantity. Systems range from single vessels or multiple parallel flow to lead/lag style applications.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Sulfatreat Process

The SulfaTreat process is a batch-type process for the selective removal of hydrogen sulfide and mercaptans from natural gas; the process is dry, using no free liquids, and can be used for all natural gas applications where a batch process is suitable.

The SulfaTreat process is a batch-type process for the selective removal of hydrogen sulfide and mercaptans from natural gas. The process is dry, using no free liquids, and can be used for all natural gas applications where a batch

process is suitable. The SulfaTreat system is a more recent development using iron oxide on a porous solid material. Unlike the iron sponge process, the SulfaTreat material is non-pyrophoric and has a higher capacity than iron sponge on a volumetric or mass basis.

In the process, the inlet gas stream enters the unit through a small inlet separator to separate out any entrained liquid, salt water, and any liquid hydrocarbon in the gas stream. The sour feed gas then passes to the top of the contactor where the SulfaTreat product (a dry, granular, free-flowing material of uniform porosity and permeability) only reacts with sulfur-containing compounds. This eliminates any side reactions with carbon dioxide that could reduce its efficiency. As the SulfaTreat bed dries out, the rate of reaction decreases. Optimum efficiency may require measuring the water content of the gas and injecting a sufficient amount of water into the influent gas to maintain a water-saturated gas and evidence of free water in the outlet gas.

The chemical cost for this processes is higher than that for iron sponge process, but this is partially offset by the ease and lower cost with which the contact tower can be cleaned out and recharged. Also, because liquids freeze and foam, antifreeze must be added in winter, and an anti-foaming agent should be available. Finally, obtaining approval to dispose of the spent chemicals, even if they are non-hazardous, is time-consuming. Two different slurry processes are described here in great detail.

See also: Gas Cleaning, Gas Processing, Gas Treating.

SulFerox Process

The SulFerox process is an iron redox process in which the hydrogen sulfide is directly oxidized to elemental sulfur while the ferric ions are reduced. These are subsequently regenerated by oxidation with air. Sulfur may be recovered as a moist filter cake or as pure liquid sulfur.

The process is mainly used for the treatment of hydrogen sulfide-containing gases such as natural gas, amine unit regenerator offgas, geothermal gas streams, and enhanced oil recovery (EOR) carbon dioxide stream.

The SulFerox process is particularly attractive for natural gas treatment when low hydrogen sulfide content and high carbon dioxide content would normally make conventional amine-based units uneconomic. The small equipment size makes the process attractive for offshore applications.

SulFerox has the following advantages over absorption-based treating processes (i) selective hydrogen sulfide removal as essentially no carbon dioxide is removed, (ii) low hydrogen sulfide content can be achieved in the treated gas (less than 5 ppm v/v), (iii) wide turndown in gas flow and/or inlet hydrogen sulfide concentration, and (iv) can operate at ambient temperature giving easy start up and shutdown.

See also: Gas Cleaning, Gas Processing, Gas Treating.

Sulfinol Process

The Sulfinol process is a combination process that uses a mixture of amines and a physical solvent (an aqueous amine and sulfolane). The solvent consists of an aqueous amine and sulfolane.

Sulfinol has a good affinity for most of the acid gases and has the ability to release these gases in the regenerator upon pressure reduction and heat application. When operating under suitable conditions, it is capable of removing twice as much acid gas as a 20% monoethanolamine (MEA) solution. This results in a considerable reduction in plant equipment size and capital cost.

This process is, in many respects, identical to the familiar amine method and its equipment components similar to those found in amine units. The main difference is that while the conventional amine process employs a fairly diluted concentration of amine in water, removing the acid gas by chemical reaction, the Sulfinol system uses a mixture of highly concentrated amine and a physical solvent removing the acid gases by physical and chemical reactions. The concentrations of the amine and the physical solvent vary with the type of feed gas in each application. Common Sulfinol mixtures are in the range of 40% amine (also called DIPA), 40% sulfolane (an organic solvent), and 20% water.

Sulfinol has a good affinity for most of the acid gases and has the ability to release these gases in the regenerator upon pressure reduction and heat application. When operating under suitable conditions, it is capable of removing twice as much acid gas as a 20% monoethanolamine solution. A Sulfinol system consists of a gas sweetening train and rich solution regeneration equipment similar to the familiar amine units.

The feed gas passes through the scrubbers after leaving the inlet separator, to remove any traces of hydrocarbon liquids and then enters the lower section of the Sulfinol absorber at a temperature of approximately 43°C (109°F). In this vessel, the ascending gas is contacted countercurrently with a stream of lean solvent fed at a point near the top. Sweetened gas leaves the contactor overhead, and after passing through a mist extractor to recover any entrained solvent, it flows to the dehydration section for further processing.

The rich solvent, withdrawn from the bottom of the contactor, is directed next to the solvent flash tank where its hydrocarbon content is flashed off at a pressure of approximately 550 kPa. The flashed vapor goes to the fuel gas contactor and after treatment with a side stream of lean solvent is used as plant fuel. The rich solvent, free of hydrocarbon derivatives, passes through a solvent to solvent heat exchanger and then to the regenerator or Sulfinol stripper to release its acid gas content.

The rich Sulfinol is contacted in the regenerator with steam vapor generated in the reboiler, and its temperature is raised to approximately 125 to 132°C (257 to 270°F). At this temperature, the Sulfinol yields its acid load which leaves the still from overhead and passes on to the reflux condenser and then to the accumulator. The hot lean solvent is cooled and pumped to the surge tank. A small side stream is directed through the filters to remove such impurities as iron oxide and various solids. The lean solvent from the surge tank is pumped again to the top of the contactor, where it repeats the cycle.

Meanwhile, the cooled acid gases from the reflux accumulator may be subjected to further treatment to remove their hydrocarbon content before they are fed to the sulfur plant. The condensed water vapor is also pumped back into the still as reflux.

Sulfinol systems are simple in operation and are considered more economical to run. Smaller size equipment can be employed in this system, resulting in fewer operational problems and lower maintenance. However, the following considerations concerning their performance and best efficiency are worthy of mention.

The correct proportion of the water content in the circulating solvent is regarded as extremely important. Since water vapor is continuously lost with the acid gas from the reflux accumulator, it must be replaced almost simultaneously, and at the same rate, in order to avoid the disintegration of the design solution mixture. Sulfinol solution of low water content will require increased power to pump and will possibly upset the operations in the contactor and stripper towers. On the other hand, a solution mixture of too high water content will not adequately absorb the acid gases from the feed stream, particularly during peak load periods.

To determine the proper water content in the mixture, Sulfinol solution tests are taken during each shift or as required. Water makeup needed is usually injected into the base of the stripper in the form of live low pressure steam. This steam is manually controlled, and with the help of a flow indicator, the correct amount of water can be added to balance the mixture. Large quantities of water, which may be needed quickly in the system, are taken care of by opening the emergency line provided for this purpose in the suction side of the reflux pump.

Another operating consideration is the degree of conditioning the solvent receives in the stripping section. Recommended H₂S content in the returning lean solvent should not be higher than 0.5 to 0.8 ppm of solvent; this can be achieved by maintaining the correct stripping pressures and temperatures in the still. Some regenerator columns may be operated under vacuum, which is considered an aid in reclaiming the Sulfinol solution and removing the high boiling degradation products. Clean filters and injection of proper amounts of chemicals into the solution is another means of maintaining cleanliness and purity of Sulfinol mixtures.

The solvent flow rates should be also constantly observed and held fairly constant in order to avoid producing residue gas off specifications. Flow rates should only be altered when the feed gas rates change, and this alteration should be done in a gentle manner. Some plants are equipped with automatic shut-down devices to shut down the feed gas in the event of low solvent flows. Restarting of these devices is done manually, and personnel should be thoroughly familiar with their operation.

Normally, foaming is not considered a serious problem in Sulfinol systems. Slugs of high-boiling liquid hydrocarbon derivatives may enter the contactor without causing the tower to foam. Pressure differential recorders, however, may be installed across the contactor and an alarm installed to warn personnel of the forthcoming conditions.

Sulfinol has shown many advantages as a gas sweetening process and has found application in a wide range of feed gases. It is an ideal method to treat acid gases containing hydrogen sulfide in excess of 5% v/v and has no difficulty in meeting the strictest pipeline specifications.

The acid gas loading capacity of Sulfinol is twice as much as MEA; consequently, the solution circulating rates are half of that required in other processes. This results in the employment of smaller size equipment and lower volumes of utility requirements. Sulfinol appears to be a stable solvent and is a mixture affected least by undesirable side reactions, considered as major problems in ethanolamine systems. It has a remarkable resistance to degradation, particularly in the presence of carbonyl sulfide and mercaptans. Sour streams, however, high in carbon dioxide and carbon disulfide, may require the use of a simple reclaiming unit.

Maintenance problems in Sulfinol processes are low, since fouling of equipment surfaces such as heat exchangers, contactor, or stripper trays and pump internals is rare. In fact, the solvent will dissolve the soft scale and sludge formations accumulated there or carried over from other stages. The life of equipment is generally longer in these systems, particularly when the normal operating conditions are constantly observed and maintained.

Some drawbacks, however, are also present in Sulfinol systems, and hydrocarbon contamination is considered as the most serious one. Sulfinol absorbs a large part of the higher-boiling hydrocarbon derivatives present in the feed stream and releases it in the still upon regeneration, only to find its way into the sulphur plant, unless it is removed in time. Hydrocarbon presence in the acid gas lowers the quality of sulfur and puts an added load to the air blowers. To prevent the hydrocarbon derivatives entrance into the sulfur plant, activated charcoal beds are usually installed in the feed line.

In sour parts of the process, where the temperature is a little higher, the corrosion rates may be more severe than elsewhere. Carbon steel or stainless steel materials are effectively employed in these areas to cope with the corrosion problem.

The Sulfinol-D process uses diisopropanolamine (DIPA), while Sulfinol-M uses methyl diethanolamine (MDEA). The mixed solvents allow for better solvent loadings at high acid gas partial pressures and higher solubility of carbonyl sulfide and organic sulfur compounds than straight aqueous amines.

The Sulfinol-D process is primarily used in cases where selective removal of hydrogen sulfide is not of primary concern, but where partial removal of organic sulfur compounds (mercaptans, RSH, and carbon disulfide) is desired, typically in natural gas and refinery applications. The Sulfinol-D configuration is also able to remove some carbonyl sulfide via physical solubility in sulfolane and partial hydrolysis to hydrogen sulfide induced by the diisopropanolamine (DIPA). However, complete removal of carbonyl sulfide by Sulfinol-D cannot be guaranteed. Unlike solvents that use other primary and secondary amines (monoethanolamine, MEA, diethanolamine, DEA) Sulfinol-D is claimed not to be degraded by these sulfur compounds.

Sulfinol-M is used when a higher degree of hydrogen sulfide selectivity is needed. Hydrogen sulfide selectivity in Sulfinol-M is controlled by the relative reaction rate of the reaction of hydrogen sulfide with methyl diethanolamine as well as by the physical solubility of hydrogen sulfide and carbon dioxide in the solvent.

The Sulfinol-X process is a regenerable amine process for acid-gas removal that uses a mixture of two or more alkanolamines – typically a base amine such as MDEA or di-isopropanolamine (Sulfinol-X) and an accelerator. The capacity for removal of carbonyl sulfide, mercaptans, and organic sulfides from gas streams is excellent because of the improved solubility of these compounds in the solvent – a mixture of water, sulfolane, and one or more alkanolamines.

The Sulfinol-X process can achieve a higher carbon dioxide loading capacity. It facilitates the design of smaller absorber columns with fewer trays.

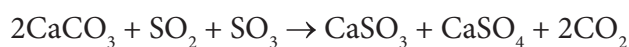
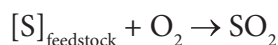
See also: Gas Cleaning, Gas Processing, Gas Treating.

Sulfur-Containing Gas Removal

Historically, the first method for removing sulfur dioxide from flue gases consisted of simple water scrubbing of the flue gas to absorb sulfur dioxide into solution, and the method was first used in London in during the 1930s. Since then, various regulatory organizations in many countries have set standards for sulfur dioxide emissions which must be met.

Sulfur dioxide represents a high percentage of the sulfur oxide pollutants generated in combustion. The removal of the sulfur dioxide from the combustion gases before they are released to the stack is essential, and a considerable number of procedures exist for flue gas desulfurization (FGD). These procedures may be classified as wet or dry depending on whether a water mixture is used to absorb the sulfur dioxide or whether the acceptor is dry.

There are a variety of processes which are designed for sulfur dioxide removal from stack gas, but scrubbing process utilizing limestone (CaCO_3) or lime [$\text{Ca}(\text{OH})_2$] slurries have found regular use for stack gas scrubbing. Use of dry limestone or dolomite (CaCO_3 , MgCO_3) within the combustor is an in situ method for sulfur dioxide removal, thereby eliminating the wet sludge from wet processes. The dry carbonate mineral is injected with the coal followed by recovery of the calcined product along with sulfite and sulfate salts:



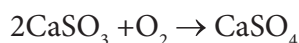
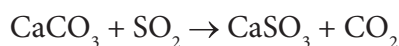
The majority of the stack gas scrubbing processes is designed to remove sulfur dioxide from the gas streams; some processes are also able to remove nitrogen oxide(s).

In addition to limestone added to the coal, the production of sulfur oxides can also be mitigated can also be removed by modifications of the combustion chamber as well as flame temperature regulation and techniques that lower combustion temperatures, such as injection of steam into the combustion which will also reduce emissions of nitrogen oxide(s).

The procedures for the removal of sulfur dioxide can be classified further as *regenerative* or *non-regenerative*, depending upon whether the chemical used to remove the sulfur dioxide can be regenerated and used again or whether the chemical is unusable and passes to disposal.

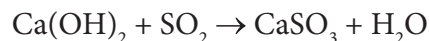
In the *wet regenerative processes*, either elemental sulfur or sulfuric acid is recovered. In the wet non-regenerative processes, using lime and/or limestone, calcium sulfite or calcium sulfate sludge is produced that is disposed. Wet scrubbing processes contact the flue gas with a solution or slurry for sulfur dioxide removal.

In a wet limestone process, the flue gas contacts a limestone slurry in a scrubber:



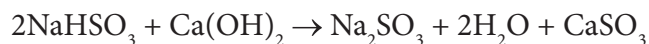
Both the sulfite and the sulfate absorb water of hydration to form the sulfite/sulfate sludge.

In a wet lime process, a gas stream containing the sulfur dioxide is reacted with a wet lime slurry to form the sulfite:



There is subsequent conversion, by oxidation, to the sulfate.

In the double alkali non-regenerative procedure, flue gas is scrubbed with a soluble alkali such as sodium sulfite which is subsequently regenerated with lime to form insoluble calcium sulfite:



After this, disposal of the calcium sulfite slurry occurs, and the spent absorbent, sodium bisulfite, is regenerated by thermal means:



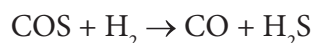
In all of these procedures, water exits the system as vapor in the flue gas.

In either the lime/limestone or sodium sulfite/lime scrubbing processes, the hydrated calcium sulfite and calcium sulfate can be of some environmental concern when the issue of disposal arises. This has, more than anything else, promoted efforts to develop alternate dry scrubbing procedures for the removal of sulfur dioxide. The dry systems have the additional advantage of reducing the pumping requirements necessary for the wet systems.

The tendency is to advocate the use of dry lime scrubbing systems, thereby producing a waste stream that can be handled by conventional fly ash removal procedures. There are also dry processes, such as the metal oxide processes, in which sulfur dioxide can be removed from gas streams by reaction with a metal oxide. These processes, which are able to operate at high temperatures (approximately 400°C; 750°F), are suitable for hot gas desulfurization without a cooling step. The metal oxides can usually be regenerated by aerial oxidation, to convert any metal sulfide(s) back to the oxide(s) or by use of a mixture of hydrogen and steam.

Membranes have found increasing industrial use in the past four decades and have also been suggested as being appropriate for the separation of hydrogen sulfide and sulfur dioxide as well as being applicable to higher temperature conditions.

The removal of carbonyl sulfide from gas streams, especially those that are destined for the manufacture of synthesis gas, is possible using:



See also: Gas Cleaning, Gas Processing, Gas Treating.

Sulfur Cycle

The sulfur cycle is the collection of processes by which sulfur moves between rocks, waterways, and living systems. The global sulfur cycle depends on the activities of metabolically and phylogenetically diverse microorganisms, most of which reside in the ocean. This involves the transformations of sulfur species through different oxidation states, which play an important role in both geological and biological processes. Steps of the sulfur cycle are: (i) mineralization of organic sulfur into inorganic forms, such as hydrogen sulfide (H_2S), elemental sulfur, as well as sulfide minerals, (ii) oxidation of hydrogen sulfide, sulfide, and elemental sulfur (S) to sulfate (SO_4^{2-}), (iii) reduction of sulfate to sulfide, and (iv) incorporation of sulfide into organic compounds (including metal-containing derivatives).

The ocean represents a major reservoir of sulfur on Earth, with large quantities in the form of dissolved sulfate and sedimentary minerals (e.g., gypsum and pyrite). Sulfur occurs in a variety of valence states, ranging from -2 (as in sulfide and reduced organic sulfur) to +6 (as in sulfate). Sulfate is the most stable form of sulfur on today's oxic Earth; weathering and leaching of rocks and sediments are its main sources to the ocean. In addition, the reduced inorganic forms of sulfur, with oxidation states of -2 and 0 (as in elemental sulfur) are quite common in anoxic environments, with sulfur compounds of mixed valence states (e.g., thiosulfate and polythionates) produced transiently. The natural release of volatile organic sulfur compounds from the ocean, mainly as dimethyl sulfide (DMS, CH_3SCH_3), transports sulfur from the ocean to terrestrial regions, and it also affects atmospheric chemistry and the climate system. While they remain important, natural sulfur emissions have currently been overtaken by anthropogenic emissions, primarily from the burning of fossil fuels.

Although sulfur rarely becomes a limiting nutrient, its turnover is critical for ecosystem function. Organic sulfur compounds fuel microbial metabolism in the upper water column, and their turnover has important consequences, for example, for the climate system. Changes in the composition of phytoplankton and bacterioplankton due to global change could thus have dramatic, but as yet poorly understood, ramifications. Sulfur-metabolizing microorganisms also fulfill essential functions in their habitats by either degrading or forming biomass (organic carbon), as exemplified by the degrading activities of sulfate-reducing bacteria in marine sediments and the formation activities of sulfur-oxidizing bacteria at deep sea hydrothermal vents. Some sulfur-oxidizing bacteria further increase ecosystem productivity by retaining nitrogen and phosphorous compounds. In the future, it will be important to improve

quantitative estimates of these processes and to learn more about their interdependencies. Such knowledge will enable us to better assess their environmental impact and their possible responses to environmental changes.

See also: Biogeochemical Cycles.

Sulfur Dioxide

Sulfur dioxide (SO_2) is a gas produced from burning sulfur-containing fuels, mainly in thermal power plants. Some industrial processes, such as production of paper and smelting of metals, produce sulfur dioxide. It is a major contributor to smog and acid rain. Sulfur dioxide can lead to lung diseases.

Acid rain is a term which is used to describe a variety of processes which might more accurately be referred to as acidic deposition. The acid rain occurs when sulfur dioxide and nitrogen oxides from the burning of fossil fuels such as petrol, diesel, and coal combine with water vapor in the atmosphere and fall as rain, snow, or fog. These gases can also be emitted from natural sources like volcanoes. Acid rain causes extensive damage to water, forest, soil resources, and even human health. It is said that it can corrode buildings and be hazardous to human health. The international scope of the problem has led to the signing of international agreements on the limitation of sulfur and nitrogen oxide emissions.

See also: Combustion.

Sulfuric Acid Treating Process

The sulfuric acid treating process is a continuous or batch method that is used to remove sulfur compounds. The treatment will also remove asphaltic materials from various refinery stocks. The acid strength varies from fuming (>100 %) to 80%; approximately 93% acid finds the most common use. The weakest suitable acid is used for each particular situation to reduce sludge formation from the aromatic and olefin hydrocarbon derivatives.

The use of strong acid dictates the use of a fairly low temperature (-4 to 10°C , 25 to 50°F), but higher temperatures (20 to 55°C , 70 to 130°F) are possible if the product is to be redistilled.

Sun

As the major source that provides energy to the Earth, the energy source of the Sun, which is the closest star to Earth, deserves some attention.

The Sun's mean distance from the Earth is on the order of 92.96 million miles, and this distance is known as an astronomical unit (abbreviated AU), which establishes the scale for measuring distances all across the solar system. The Sun, a huge sphere of mostly ionized gas, supports life on Earth, and, moreover, the connection and interactions between the Sun and Earth drive the seasons, ocean currents, weather, and climate.

The Sun has no solid surface and is held together by gravitational attraction, producing immense pressure and temperature at its core and has six regions which are (i) the core, (ii) the radiative zone, (iii) the convective zone, (iv) the visible surface, which is also called the photosphere, (v) the chromosphere, and (iv) the outermost region, the corona. The Sun has no solid surface.

At the core, the temperature is on the order of $15,000,000^\circ\text{C}$ ($27,000,000^\circ\text{F}$), which is sufficient to sustain thermonuclear fusion. The energy produced in the core powers the Sun and produces essentially all the heat and light that are received by the Earth. Energy from the core is carried outward by radiation, which moves around the radiative zone, taking approximately 170,000 years to get from the core to the convective zone. The temperature drops below 2 million degrees Celsius (3.5 million degrees Fahrenheit) in the convective zone, where large bubbles of hot plasma (a soup of ionized atoms) move upwards. The photosphere 300-mile-thick region, from which most of the radiation of the Sun escapes outward and is detected as the sunlight that is observed on Earth approximately eight minutes after it leaves the Sun.

Sunspots in the photosphere are areas with strong magnetic fields that are cooler, and thus darker, than the surrounding region. Sunspot numbers fluctuate every 11 years as part of the Sun's magnetic activity cycle. Also connected to this cycle are bright solar flares and huge coronal mass ejections that blast off of the Sun. The temperature of the photosphere is on the order of 5,500°C (10,000°F). Above the photosphere lie the tenuous chromosphere and the corona, and the visible light from these top regions is usually too weak to be seen against the brighter photosphere, but during total solar eclipses, when the Moon covers the photosphere, the chromosphere can be seen as a red rim around the Sun while the corona forms a beautiful white crown with plasma streaming outward, forming the points of the crown.

Above the photosphere, temperature increases with altitude, reaching as high as 2,000,000°C (3,500,000°F). The source of coronal heating has been a scientific mystery for more than 50 years.

See also: Solar Furnace – The Sun.

Sunflowers

Sunflowers are widely adapted in the United States but are most commonly grown in the western and northern Corn Belt. Sunflowers have been grown in localized areas of the Southeast for 15 or 20 years, primarily where there are specialty markets for the seed. Some cultivars of sunflowers have a short growing season, and the crop has potential in double-cropping scenarios either as the first or second crop.

Sunflower oil, extracted from the seeds, is used for cooking, as carrier oil, and to produce margarine and biodiesel. A range of sunflower varieties exist with differing fatty acid compositions. Some high oleic acid types contain a higher level of healthy monounsaturated fats in their oil than even olive oil.

Sunflower is a high oil content seed, and average yields can produce 600 pounds of oil per acre, considerably more than soybeans. There is a great deal of interest from local areas for construction of small processing facilities for sunflower biodiesel production. It is most important that processing equipment be analyzed very carefully for small press only facilities. In most cases, a portion of the oil is left in the by-product meal, thereby reducing economic efficiency.

Biodiesel can be produced from sunflower oil through a chemical process (transesterification). It is recommended that the sunflower oil be refined and de-waxed before blending it with diesel fuel.

See also: Biodiesel, Transesterification, Vegetable Oil.

Supercritical Fluid

A supercritical fluid is any substance at a temperature and pressure above the critical point where distinct liquid and gas phases do not exist, and which can effuse through solids like a gas and dissolve materials like a liquid.

Furthermore, there is no surface tension in a supercritical fluid, as there is no liquid/gas phase boundary. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, thereby allowing many properties of a supercritical fluid to be adjusted to be more liquid-like or more gas-like. All supercritical fluids are completely miscible with each other, so for a mixture, a single phase can be guaranteed if the critical point of the mixture is exceeded. The critical point of a binary mixture can be estimated as the arithmetic mean of the critical temperatures and pressures of the two components:

$$T_{c(mix)} = (\text{mole fraction } A) \times T_{cA} + (\text{mole fraction } B) \times T_{cB}$$

$T_{c(mix)}$ is the critical temperature of the mixture, A is component A , T_{cA} is the critical temperature of component A , B is component B , and T_{cB} is the critical temperature of component B . For greater accuracy, the critical point can be calculated using equations of state, and other properties, such as density, can also be calculated using equations of state.

Supercritical Fluid Extraction

Supercritical fluid extraction is the use as an extraction solvent of a material at a pressure and temperature above its vapor-liquid critical point. The process is very similar to liquid-liquid extraction. The critical point of the solvent is the temperature above which it cannot be liquefied, no matter how high the applied pressure. The corresponding vapor pressure at the critical temperature is called the critical pressure and is usually between 500 and 1,200 psig for light hydrocarbon gases, light freons, and carbon dioxide. The viscosity and diffusion properties of a supercritical solvent are much like those of a gas. However, the density, and thus the molecular interactions leading to solute solubility, are more like those of a liquid. These molecular interactions achieve the solubilization of high-molecular-weight solutes into a supercritical gas phase at temperatures well below the boiling point of the solute. This permits use of the supercritical gas as an extraction solvent for high-boiling-point heat-sensitive materials. It should be remembered that while this discussion is limited to the *extraction* application of supercritical fluids, once the solute is in the supercritical carrier phase, it can be treated by adsorbents, separated by chromatography, and subjected to other separation processes.

Most, if not all, of the separations possible with supercritical gas solvents could also be made with liquid solvents either well below or in the vicinity of their critical points. What is it then that drives the increasing application of supercritical gas extraction? It is the easier and less expensive solvent recovery, coupled with essentially complete solvent removal from the products, because of (i) the availability of non-toxic supercritical gas solvents such as carbon dioxide, (ii) the ability to process essentially non-volatile materials at moderate temperatures, and (iii) the low phase viscosities and high density differences between the phases, which enhance effective mass transfer and phase disengagement.

The solubility of solutes in the supercritical fluid increases as the density of the supercritical fluid is increased. Thus, operation at high pressure gives high solubilities in the supercritical solvent. Reduction of pressure on the supercritical gas phase decreases solubility and precipitates out part of the solute. This phenomenon can be used to perform intermediate fractionation of solute by reducing pressure in steps during solvent recovery. The supercritical solvent can be recovered from both the extract and raffinate merely by lowering pressure below the critical and letting the gaseous solvent flash off. Thus, by choosing a material having a low critical point, an effective extraction solvent of low viscosity, high solubilizing power, rapid mass transfer, and easy solvent recovery is obtained. The penalty for these benefits is the requirement for (i) operation at moderate-to-high pressure in pressure vessels and (ii) a compressor in the solvent recycle loop.

Relatively mild operating temperatures are possible for supercritical extractions using light hydrocarbons, light freons, or carbon dioxide as solvents. These range from 50 to about 120°C (250°F at pressures from 600 to several thousand psi). The use of water as a supercritical solvent requires temperatures above 430°C (705°F) and pressures above 3,200 psi. Thus, supercritical water finds more use as a medium for incineration by oxidation than as a solvent for extraction without conversion.

See also: Liquid-Liquid Extraction, Solvent Extraction.

Super-Slagging Combustor

The super-slagging combustor invokes the concept of burning coal (to produce a low heat-content gas) within a bed of molten coal-ash slag fluxed with limestone; the sulfur in the coal reacts with the lime to form calcium sulfide. Thus, if such a super-slagging combustor were incorporated into a steam-generating boiler furnace with controlled addition of secondary air, the result might be a direct combustion system that produces flue gas with no sulfur or nitrogen oxides through staged combustion and maintains particulate emissions at a minimum. However, thermochemical calculations have shown that the product gas must be in equilibrium with excess carbon if sulfur is to be detained by the calcium oxide fluxed slag at 1,540°C (2,800°F) and that under even moderately oxidizing conditions, sulfur would not be absorbed. This has been demonstrated in preliminary tests where the sulfur in the product gas can be as little as of the sulfur in the feed gas.

See also: Combustion.

Surface Tension

Surface tension is a consequence of the imbalances in attractive forces between molecules and is related to the decrease in surface energy that results from decreasing surface area. At the surface, a layer forms in which the molecules are strongly bonded, thereby making it harder to penetrate the surface of the liquid than to move submersed objects. Stronger interactions between molecules result in higher values of surface tension, while lower values indicate that the molecules are not interacting as strongly. The dimensions for surface tension are expressed as force per unit length or energy per unit area. The surface tension of water is 72 dynes/cm at 25°C, indicating that it would take a force of 72 dynes to break a surface film of water 1 cm in length. Surface tension varies between liquids and is affected by temperature.

Surface tension is responsible for a broad range of phenomena. Surface tension impacts the shape of droplets, and allows for bubble formation.

See also: Capillary Forces.

Suspended Particulate Matter

Suspended particulate matter (SPM) is a general term used to describe particulate matter in gas streams, such as certain types of fine ash and dust. The particles are small pieces of matter measuring approximately 2.5 microns. One type of air pollution is the release of particles into the air from burning fuel for energy. Diesel smoke is a good example of this particulate matter. This type of pollution is sometimes referred to as black carbon pollution. The exhaust from burning fuels in automobiles, homes, and industries is a major source of pollution in the air.

See also: Particulate Matter.

Sustainability

Sustainability is an ecosystem condition in which biodiversity, renewability, and resource productivity are maintained. Thus, the term sustainability means meeting human needs without compromising the ability of future generations to meet their needs. In addition to natural resources, humans also need social and economic resources. In fact, sustainability is not just environmentalism, and embedded in the definition of sustainability, there are also considerations of social equity and economic development. In fact, while the concept of sustainability is a relatively new idea, the sustainability movement comes from the basics in social justice, conservationism, internationalism, and other past movements. By the end of the 20th century, many of these ideas had come together in the call for sustainable development.

In terms of environmental sustainability, ecological integrity is maintained; all of Earth's environmental systems are kept in balance, while the natural resources within them are consumed by humans at a rate where they are able to replenish themselves.

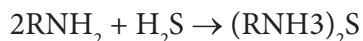
Economic sustainability means that human communities across the globe are able to maintain their independence and have access to the resources that they require, financial and other, to meet their needs. Economic systems are intact, and activities are available to everyone, such as secure sources of livelihood.

Finally, social sustainability is the concept that universal human rights and basic necessities are attainable by all people, who have access to enough resources in order to keep their families and communities healthy and secure. Healthy communities have just leaders who ensure personal, labor, and cultural rights are respected and all people are protected from discrimination.

See also: Environmental Ethics.

Sweetening Processes

Many chemical processes are available for sweetening natural gas (Table S-4). For decades, the amine (olamine) process (also known as the Girdler process) has been the most widely used method for removal of hydrogen sulfide:



In this equation, R is mono, di, or tri-ethanol, N is nitrogen, H is hydrogen, and S is sulfur.

The recovered hydrogen sulfide gas stream may be: (1) vented, (2) flared in waste gas flares or modern smokeless flares, (3) incinerated, or (4) utilized for the production of elemental sulfur or sulfuric acid. If the recovered hydrogen sulfide gas stream is not to be utilized as a feedstock for commercial applications, the gas is usually passed to a tail gas incinerator in which the hydrogen sulfide is oxidized to sulfur dioxide and water for further processing of the sulfur dioxide.

Table S-4 Summary of the natural gas sweetening processes.

Iron-Sponge Sweetening
Reaction: $2\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{S} \rightarrow 2\text{Fe}_2\text{S}_3 + 6\text{H}_2\text{O}$ Regeneration: $2\text{Fe}_2\text{S}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 6\text{S}$ A batch process; most applicable for small gas volume with low content of hydrogen sulfide; operating temperature of the vessel <120°F (<49°C).
Alkanolamine Sweetening
Reaction: $\text{MEA} + \text{H}_2\text{S} \rightarrow \text{MEA-hydrosulfide} + \text{heat}$ $\text{MEA} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{MEA-carbonate} + \text{heat}$ Regeneration: $\text{MEA-hydrosulfide} + \text{heat} \rightarrow \text{MEA} + \text{H}_2\text{S}$ $\text{MEA-carbonate} + \text{heat} \rightarrow \text{MEA} + \text{H}_2\text{O} + \text{CO}_2$ Alkanolamine: organic compounds including monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA); not selective and have to be designed for total acid-gases removal; operating $p > 125$ psi for DEA; can absorb most of the acid gases and meet the specified pipeline requirement.
Glycol/Amine Process
A solution composed of 10-30% w/w MEA, 45-85% w/w glycol, and 5-25% w/w water for the simultaneous removal of water vapor, hydrogen sulfide, and carbon dioxide; the process flow scheme is essentially the same as that for MEA; applicable when low dew point is not required; there can be losses of MEA due to vaporization in the regeneration stage at high temperature.
Sulfinol Process
The solvent [composed of sulfolane, diisopropanolamine (DIPA), and water] acts as the physical (sulfolane) and chemical (DIPA) solvent; there is the benefit of low solvent circulation rates, smaller equipment, and lower cost; on the other hand, there can be absorption of high-molecular-weight hydrocarbon derivatives and aromatic derivatives.
Chemsweet Process and Zinc Oxide Process
Reaction: $\text{ZnAc}_2 + \text{H}_2\text{S} \rightarrow \text{ZnS} + 2\text{HAc}$, $\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$ Regeneration: $\text{ZnO} + 2\text{HAc} \rightarrow \text{ZnAc}_2 + \text{H}_2\text{O}$ Can be used to treat gas with a high concentration of hydrogen sulfide; operating p on the order of 89 to 1,415 psi; should not be used when the mercaptan concentration is in excess of 10% v/v hydrogen sulfide in the gas stream – mercaptans react with ZnO and forms Zn(OH)RH which will form a sludge and possibly cause foaming problems.

See also: Recovery Processes.

Sweet Potatoes

Sweet potatoes can produce 40% more alcohol per unit area than Jerusalem artichoke and two to four times as much as the other carbohydrate crops.

In addition to a high-yield capability, sweet potatoes have several other advantages. They can be planted and harvested mechanically and have good storage life so that an alcohol production facility could be supplied with feedstock over a period of several months. Many of the highest-yielding cultivars of sweet potatoes, including Jewel, are marketed for food and are also readily eaten by cattle. Thus, there could be considerable flexibility in marketing a sweet potato crop and in using those which might not find a ready sale. Dry weather at transplanting may hinder stand establishment unless irrigation is available. Harvesting is difficult unless sweet potatoes are grown on sandy or loamy soils.

Sweet potatoes have the ability to yield two to three times as much carbohydrate for fuel ethanol production as field corn grown in the same areas. In fact, the sweet potato carbohydrate yields approached the lower limits of those produced by sugarcane, the highest-yielding ethanol crop.

This leaves sweet potatoes with the potential to be a viable alternative as biofuel source. Although they require less pesticides and fertilizer than corn, planting and harvesting incur higher labor costs.

See also: Starch Crops.

Switchgrass

Switchgrass (*Panicum virgatum*) is a perennial sod-forming grass with thick strong stems. It is a perennial warm season bunchgrass that is native to North America, where it occurs naturally from Canada southwards into the United States and Mexico. Switchgrass is one of the dominant species of the central North American tallgrass prairie and can be found in prairie remnants (grassland areas in the Western and Midwestern United States and Canada that remain, to some extent, undisturbed), in native grass pastures, and naturalized along roadsides. There are, in fact, many perennial crops (grass and tree species) that show high potential for production of cost-competitive cellulosic biomass. The “best” crop for a given area can only be determined by local soil and climate conditions and the desired end-use.

Switchgrass can be viewed as a surrogate for many “perennial energy crops” when doing biomass supply analysis. Other perennial energy crops that might be preferred in some situations include other thin-stemmed grasses, such as Reed Canary grass or Big Bluestem grass, or thick-stemmed grasses with rhizomes, such as *Miscanthus*, Energy cane, or *Arundo* (all may sometimes be marketed as E-Grass); trees grown as single stem row crops, such as poplars, eucalyptus, silver maple, sweetgum, and sycamore, or trees grown as multiple stem row crops such as willow or poplar coppice. Some annual crops are also being evaluated as dedicated energy crops including corn, sorghum, and kenaf (a woody annual crop), because of high yields. The perennial crops will normally show better environmental performance due to lower chemical requirements and better erosion control. The cost of production of energy crops is sensitive to yield; thus, the development of better energy crops involves traditional genetic selection and/or molecular genetics. It is also extremely important to select appropriate sites and optimize agronomic or silvi-cultural management techniques to eliminate weed competition and assure that adequate nutrients and water are available (but without overfertilizing or irrigating).

The advantages of switchgrass as an energy crop are that it is fast-growing, remarkably adaptable, and high-yielding. Further advantages of Switchgrass are that it can be harvested, using conventional equipment, either annually or semi-annually for 10 years or more before replanting is needed and that it is able to reach deep into the soil for water and use water very efficiently. Further advantages of switchgrass are that it can be harvested, using conventional equipment, either annually or semi-annually for 10 years or more before replanting is needed and that it is able to reach deep into the soil for water and use water very efficiently. Besides showing great promise as an energy crop for energy production, switchgrass also restores vital organic nutrients to farmed-out soils, and with its extensive network of stems and roots (the plants extend nearly as far below ground as above), it is also a valuable soil stabilization plant.

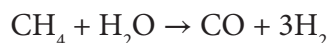
Switchgrass has the potential to be a versatile bioenergy feedstock since the energy content is comparable to that of wood with significantly lower initial moisture content. Switchgrass is very suitable substrate and produces high ethanol yield using current simultaneous saccharification and fermentation technology. Extensive analysis of ash and alkali content of switchgrass indicates that it typically has relatively low alkali content and should have low slagging potential in coal-fired combustion systems. As an agro-fiber source for pulping, switchgrass has a relatively high cellulose content, low ash content, and good fiber length-to-width ratios. Switchgrass reaches its full yield potential after the third year planted, producing approximately 6 to 8 tons per acre; that is 500 gallons of ethanol per acre.

The utilization of energy crops such as *switchgrass* (*Panicum virgatum* L., Poaceae) is a concept with great relevance to current ecological and economic issues on a global scale. Development of a significant national capacity to utilize perennial forage crops, such as switchgrass as biofuels, could provide an important new source of energy from perennial cropping systems, which are compatible with conventional farming practices, and would help reduce degradation of agricultural soil.

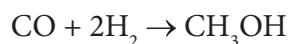
See also: Cordgrass, Energy Crops, Miscanthus, Reed Canary Grass, Short Rotation Coppice.

Synthesis Gas

Synthesis gas (also called syngas) is a mixture of carbon monoxide (CO) and hydrogen (H₂) that is manufactured by steam reforming natural gas. Some carbon dioxide is almost always inevitably produced.



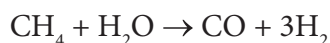
This gas is an extremely important precursor for the synthesis of methanol, hydrogen, ammonia and other products. In particular, methane can be converted to synthesis gas and naphtha can then be produced from this mixture by the Fischer-Tropsch process. Naphtha is currently produced in Sasol, South Africa and in Malaysia using this technology. Methanol can be produced from synthesis gas using the methanol-to-gasoline (MTG) process:



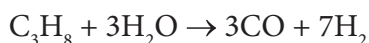
The synthesis gas produced using existing methods accounts for approximately 60% of the total conversion cost of natural gas to gasoline. Thus, natural gas is an excellent candidate as an abundant alternative energy source.

The trend to increase the number of hydrogenation (hydrocracking and/or hydrotreating) processes in refineries coupled with the need to process the higher-boiling oils, which require substantial quantities of hydrogen for upgrading, has resulted in vastly increased demands for this gas. Part of the hydrogen needs can be satisfied by hydrogen recovery from catalytic reformer product gases, but other external sources are required. Most of the external hydrogen is manufactured either by steam-methane reforming or by oxidation processes. However, other processes, such as steam-methanol interaction or ammonia dissociation, may also be used as sources of hydrogen. Electrolysis of water produces high-purity hydrogen, but the power costs may be prohibitive.

The steam-methane reforming is a continuous catalytic process that has been employed for synthesis gas production and in some refineries, hydrogen production over a period of several decades. The major reaction is the formation of carbon monoxide and hydrogen from methane and steam:



Higher-molecular-weight feedstocks (such as propane and other hydrocarbon constituents of natural gas) may also yield carbon monoxide and hydrogen that can be adjusted to fit the required ratio for synthesis gas:



That is,



In the actual process, the feedstock is first desulfurized by passage through activated carbon, which may be preceded by caustic and water washes. The desulfurized material is then mixed with steam and passed over a nickel-based catalyst (730–845°C, 1,350 to 1,550°F and 400 psi). Effluent gases are cooled by the addition of steam or condensate to approximately 370°C (700°F), at which point (if hydrogen is the desired product) carbon monoxide reacts with steam in the presence of iron oxide in a shift converter to produce carbon dioxide and hydrogen. The carbon dioxide is removed by amine washing; the hydrogen is usually a high-purity (>99%) material.

Another synthesis gas generation process is a continuous, non-catalytic process that produces carbon monoxide and hydrogen by partial oxidation of gaseous or liquid hydrocarbon derivatives. A controlled mixture of preheated feedstock and oxygen is fed to the top of the reactor, where carbon dioxide and steam are the primary products. A secondary reaction between the feedstock and the gases forms carbon monoxide and hydrogen.

If necessary for hydrogen production only, the effluent is then led to a shift converter with high-pressure steam, where carbon monoxide is converted to carbon dioxide with the concurrent production of hydrogen at the rate of 1 mole of hydrogen for every mole of carbon dioxide. Reactor temperatures vary from 1,095 to 1,480°C (2,000 to 2,700°F) and pressures from atmospheric to more than 1,500 psi. Gas purification depends on the use of the gas.

See also: Fischer-Tropsch, Synthesis Gas.

Synthesis Gas – Fermentation

Anaerobic bacteria are able to grow on synthesis gas components, thus forming acetate and ethanol. The bacteria conversion has the advantages of high selectivity, no thermal equilibrium (because of irreversible ingestion of synthesis gas), and fewer problems with catalyst poisoning.

The bacteria culture has to be able to convert carbon dioxide, carbon monoxide, and hydrogen into ethanol. Many of the organisms are either mesophiles or thermophiles with temperature optimums ranging from room temperature to 90°C (195°F). A fairly rich medium is typically required, but high operating temperatures, low carbohydrate levels, low pH, and high carbon monoxide levels (which are inhibitory to methanogens) reduce the risk of contamination.

In contrast to many other synthesis gas-based processes, synthesis gas fermentation performance is not tied to a specific ratio of hydrogen to carbon monoxide. While the organisms generally prefer carbon monoxide to hydrogen, both carbon monoxide and hydrogen/carbon dioxide mixtures can be simultaneously converted.

The bacterium *Clostridium ljungdahlii* can be used where the reactants are carbon dioxide, carbon monoxide, and hydrogen reacting in an aqueous phase where pressure is less than 30 psi and the temperature is 35 to 37°C (95 to 99°F).

The ratio between ethanol to acetate produced is dependent upon fermentation reaction conditions. The production of acetic acid leads to a decreased pH, together with a higher concentration of acetate ions. This inhibits the organisms, in order to avoid further inhibition as the organisms switch to ethanol production. The pH is normally kept at 4.5 in ethanol production.

With a hydrogen/carbon monoxide ratio of 2, the reaction indicates that water and ethanol are the only theoretical products, but the ratio is not of major importance as the bacteria prefer carbon monoxide. Additionally, carbon monoxide and hydrogen shift reactions to improve the ratio are thus not necessary. The ethanol is toxic to the bacteria, resulting in a need to hold the ethanol concentrations below 3% in the reactor.

The biocatalytic reaction has the advantages of high yields and a high selectivity. The only products are ethanol, carbon dioxide, and water, thus avoiding upgrading, cracking, or separating processes of lower-grade products.

See also: Fermentation, Synthesis Gas.

Synthesis Gas – Fischer-Tropsch Process

In principle, synthesis gas can be produced from any hydrocarbon feedstock, which include natural gas, naphtha, residual oil, crude oil coke, coal, biomass, and municipal or industrial waste. The product gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products. In addition, synthesis gas may also be used to produce a variety of products, including ammonia, and methanol.

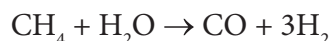
Of all of the carbonaceous materials used as feedstocks for gasification process, coal represents the most widely used feedstocks and, accordingly, about which the knowledge base is voluminous. In fact, gasification of coal has been a commercially available proven technology (2013a, 2013b). The modern gasification processes have evolved from three first-generation process technologies: (i) Lurgi fixed bed reactor, (ii) high-temperature Winkler fluidized bed reactor, and (iii) Koppers-Totzek entrained flow reactor. In each case, steam/air/oxygen are passed through heated coal which may be a fixed bed, a fluidized bed, or entrained in the gas. Exit gas temperatures from the reactor are 500°C (930°F), 900 to 1,100°C (1,650 to 2,010°F), and 1300 to 1,600°C (2,370 to 2,910°F), respectively. In addition to the steam/air/oxygen mixture being used as the feed gases, steam/oxygen mixtures can also be used in which membrane technology and a compressed oxygen-containing gas is employed.

In addition, low-value or negative-value materials and wastes such as crude oil coke, refinery residua, refinery waste, municipal sewage sludge, biomass, hydrocarbon contaminated soils, and chlorinated hydrocarbon by-products have all been used successfully in gasification operations. In addition, synthesis gas is used as a source of hydrogen or as an intermediate in producing a variety of hydrocarbon products by means of the Fischer-Tropsch synthesis (Chadeesingh, 2011). In fact, gasification to produce synthesis gas can proceed from any carbonaceous material, including biomass and waste.

There are different sources for obtaining synthesis gas. It can be produced by steam reforming or partial oxidation of any hydrocarbon ranging from natural gas (methane) to crude oil residua. It can also be obtained by gasifying the carbonaceous feedstock to a medium Btu gas (medium Btu gas consists of variable amounts of carbon monoxide, carbon dioxide, and hydrogen and is used principally as a fuel gas).

The first step in the process is feedstock preparation which may include unit operations such as (i) size reduction, (ii) screening, and (iii) slurring. The design of the feedstock preparation section depends on the properties of the raw material feed and on the requirements of the gasification technology that is selected. For example, preparing any form of crude oil resid, biomass, or waste for gasification is different to the preparation of bituminous coal for the gasifier, and the type of gasifier suitable for the gasification may also (or more than likely) be feedstock dependent.

Once the feedstock is prepared for the gasifier, the major route for producing synthesis gas is the steam reforming of natural gas over a promoted nickel catalyst at temperatures on the order of 800°C (1,470°F):



In some countries, synthesis gas is mainly produced by steam reforming naphtha. Because naphtha is a mixture of hydrocarbon derivatives ranging approximately from C5 to C10, the steam reforming reaction may be represented using n-heptane:



As the molecular weight of the hydrocarbon increases (lower H/C feed ratio), the hydrogen/carbon monoxide (H_2/CO) product ratio decreases. The hydrogen/carbon monoxide product ratio is approximately 3 for methane, 2.5 for ethane, 2.1 for heptane, and less than 2 for heavier hydrocarbon derivatives. The non-catalytic partial oxidation of hydrocarbon derivatives is also used to produce synthesis gas, but the hydrogen/carbon monoxide ratio is lower than from steam reforming. In practice, this ratio is even lower than what is shown by the stoichiometric equation because part of the methane is oxidized to carbon dioxide and water. When resids are partially oxidized by oxygen and steam at 1,400 to 1,450°C (2,550 to 2,640°F) and pressures on the order of 11,500 to 13,000 psi, the gas consists of equal parts of hydrogen and carbon monoxide.

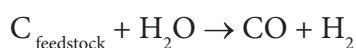
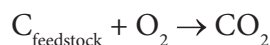
See also: Synthesis Gas, Synthesis Gas – Fermentation, Synthesis Gas – Production.

Synthesis Gas – Production

In addition to the fermentation process, the gasification to produce synthesis gas can proceed from almost any organic material, including renewable resources such as biomass and plastic waste. The chemistry of the process for producing synthesis gas can be represented simply as:



Thus:



The products designated as synthesis fuels include low-to-high-boiling hydrocarbon derivatives and methanol. Also, the high-boiling products (including wax products) can also be used as feedstocks for gas production.

In addition, the actual process is described as comprising three components: (i) synthesis gas generation, (ii) waste heat recovery, and (iii) gas processing. Within each of the above three listed systems are several options. For example, synthesis gas can be generated to yield a range of compositions ranging from high-purity hydrogen to high-purity carbon monoxide. Two major routes can be utilized for high-purity gas production: (i) pressure swing adsorption and (ii) utilization of a cold box, where separation is achieved by distillation at low temperatures. In fact, both processes can also be used in combination as well. Unfortunately, both processes require high capital expenditure. However, to address these concerns, research and development are ongoing, and successes can be measured by the demonstration and commercialization of technologies such as permeable membrane for the generation of high-purity hydrogen, which in itself can be used to adjust the hydrogen/carbon monoxide ratio of the synthesis gas produced.

The resulting synthesis gas burns cleanly into water vapor and carbon dioxide or, alternatively, the gas may be converted to methane via the Sabatier reaction as well as to or to a kerosene liquid via the Fischer-Tropsch process. Inorganic components of the feedstock, such as metals and minerals, are trapped in an inert and environmentally safe form as a carbonaceous char that may be used as a fertilizer. The synthesis gas produced in large waste-to-energy gasification facilities is used as fuel to generate electricity.

A modified version of steam reforming known as autothermal reforming, which is a combination of partial oxidation near the reactor inlet with conventional steam reforming further along the reactor, improves the overall reactor efficiency and increases the flexibility of the process. Partial oxidation processes using oxygen instead of steam also found wide application for synthesis gas manufacture, with the special feature that they could utilize low-value feedstocks such as heavy crude oil residua. In recent years, catalytic partial oxidation employing short reaction times (milliseconds) at high temperatures (850 to 1,000°C; 1,560 to 1,830°F) is providing still another approach to synthesis gas manufacture. Nearly complete conversion of methane, with close to 100% selectivity to hydrogen and carbon dioxide, can be obtained with a rhenium monolith under well-controlled conditions. Experiments on the catalytic partial oxidation of *n*-hexane conducted with added steam give much higher yields of hydrogen than can be obtained in experiments without steam, a result of much interest in obtaining hydrogen-rich streams for fuel cell applications.

The route for a carbonaceous feedstock to synthetic automotive fuels, as practiced by SASOL, is technically proven, and a series of products with favorable environmental characteristics are produced. As is the case in essentially all conversion processes, for carbonaceous feedstocks where air or oxygen is used for the utilization or partial conversion of the energy in the coal, the carbon dioxide burden is a drawback as compared to crude oil.

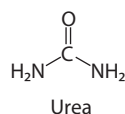
The uses of synthesis gas include use as a chemical feedstock and in gas-to-liquid processes, which use Fischer-Tropsch chemistry to make liquid fuels as feedstock for chemical synthesis, as well as being used in the production of fuel additives, including diethyl ether and methyl *t*-butyl ether (MTBE), acetic acid, and its anhydride, synthesis gas

could also make an important contribution to chemical synthesis through conversion to methanol. There is also the option in which stranded natural gas is converted to synthesis gas production followed by conversion to liquid fuels.

Synthesis Gas – Products

Synthesis gas is an important intermediate. The mixture of carbon monoxide and hydrogen is used for producing methanol and a host of other products. Synthesis gas is also used to synthesize a wide variety of hydrocarbon derivatives ranging from gases to naphtha to gas oil using Fischer-Tropsch technology. This process may offer an alternative future route for obtaining olefin derivatives and chemicals.

Synthesis gas is a major source of hydrogen, which is used for producing ammonia. Ammonia is the host of many chemicals such as urea, ammonium nitrate, and hydrazine. Carbon dioxide, a by-product from synthesis gas, reacts with ammonia to produce urea (H_2NCONH_2).

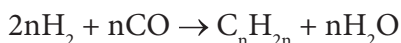


Urea (also known as carbamide) serves an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water, and, dissolved in water, it exhibits neither an acid nor an alkali. It is formed in the liver by the combination of two ammonia molecules (NH_3) with a carbon dioxide (CO_2) molecule. It is widely used in fertilizers as a source of nitrogen and is an important raw material for the chemical industry.

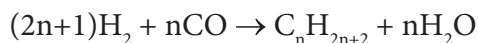
Most of the production of hydrocarbon derivatives by the Fischer-Tropsch method uses synthesis gas produced from sources that yield a relatively low hydrogen/carbon monoxide ratio, such as typical in coal gasifiers. This, however, does not limit this process to low hydrogen/carbon monoxide gas feeds. The only large-scale commercial process using this technology is in South Africa, where coal is an abundant energy source. The process of obtaining liquid hydrocarbon derivatives from coal through the Fischer-Tropsch process is termed indirect coal liquefaction which was originally intended for obtaining liquid hydrocarbon derivatives from solid fuels. However, this method may well be applied in the future to the manufacture of chemicals through cracking the liquid products or by directing the reaction to produce more olefin derivatives.

The reactants in Fischer-Tropsch processes are carbon monoxide and hydrogen. The reaction may be considered a hydrogenative oligomerization of carbon monoxide in presence of a heterogeneous catalyst. The main reactions occurring in Fischer-Tropsch processes are:

(i) Olefin derivatives:



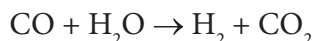
(ii) Paraffin derivatives:



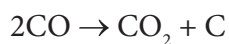
(iii) Alcohol derivatives:



The coproduct water reacts with carbon monoxide (the shift reaction), yielding hydrogen and carbon dioxide:



The gained hydrogen from the water shift reaction reduces the hydrogen demand for Fischer-Tropsch processes. Water-gas shift proceeds at approximately the same rate as the Fischer-Tropsch reaction. Another side reaction also occurring in Fischer-Tropsch process reactors is the disproportionation of carbon monoxide to carbon dioxide and carbon:



This reaction is responsible for the deposition of carbon in the reactor tubes in fixed-bed reactors and reducing heat transfer efficiency.

Fischer-Tropsch technology is best exemplified by the SASOL projects in South Africa. After the carbonaceous feedstock is gasified to a synthesis gas mixture, it is purified in a Rectisol unit. The purified gas mixture is reacted in a Synthol unit over an iron-based catalyst. The main products are gasoline, diesel fuel, and jet fuels. By-products are ethylene, propylene, alpha olefin derivatives, sulfur, phenol, and ammonia which are used for the production of downstream chemicals. However, the exact mechanism is not fully established. One approach assumes a first-step adsorption of carbon monoxide on the catalyst surface followed by a transfer of an adsorbed hydrogen atom from an adjacent site to the metal carbonyl (M-CO). The polymerization continues (as in the last three steps shown above) until termination occurs and the hydrocarbon is desorbed. The last two steps shown above explain the presence of oxygenated derivatives in Fischer-Tropsch products.

Alternatively, an intermediate formation of an adsorbed methylene on the catalyst surface through the dissociative adsorption of carbon monoxide has been considered. The formed metal carbide (M-C) is then hydrogenated to a reactive methylene metal species. The methylene intermediate abstracts a hydrogen and is converted to an adsorbed methyl. Reaction of the methyl with the methylene produces an ethyl-metal species. Successive reactions of the methylene with the formed ethyl produce a long chain-adsorbed alkyl. The adsorbed alkyl species can either terminate to a paraffin by a hydrogenation step or to an olefin by a dehydrogenation step. The carbide mechanism, however, does not explain the formation of oxygenate derivatives in Fischer-Tropsch products.

See also: Fischer-Tropsch Process, Fischer-Tropsch Products, Synthesis Gas – Fermentation.

Gas-to-liquids processing is similar to oil refining, since a number of products is obtained (Table S-5). Thus, gas-to-liquids synthesis can be regarded as an alternative refinery, run on feedstocks other than oil – natural gas, coal, or biomass. The total energy efficiency of gas-to-liquids processing is lower than that of oil refining (80% versus 85 to 90%), but the 20% gas-to-liquids thermal losses can be partly recovered via heat integration in the process units.

Table S-5 Examples of products from synthesis gas.

	Primary products	Secondary products
Synthesis gas	Ammonia	Amines Fertilizers
	Butanol	Butylene
	Ethanol	Aldehydes Ethylene Ketones
	Hydrocarbons	Naphtha (gasoline) Kerosene (diesel fuel)
	Methanol	Acetic acid Dimethyl ether Formaldehyde
	Olefins	Polymers
	Propanol	Propylene
	Wax	

Gas-to-liquids processing has an important technological difference with oil refining. The optimum oil refining output by fractions is spread among a number of products, is relatively constant, and can vary within relatively narrow margins. Conversely, the optimum breakdown of fractions in gas-to-liquids synthesis is more flexible and can be optimized to a larger extent versus certain products, most often versus middle distillates. Another feature of gas-to-liquids processing is that the higher-boiling fractions consist of high-quality lubricants and waxes ($<C_{20}$), but not of high-boiling fuel oils like in oil refining.

Gas-to-liquids lubricants and waxes could find a ready market, including in the food industry, while the market for high-boiling fuel oils is generally less profitable, along with the environmental burdens they cause. An additional and important environmental advantage of gas-to-liquids products is that, unlike oil derivatives, they are quickly biodegradable – the degradation rate of gas-to-liquids diesel reaches 60% within only 28 days in anaerobic conditions.

Gas-to-liquids products consist almost entirely of linear paraffins ($C_n H_{2n+2}$), with less than 5% aromatics on mass basis, compared to 10 to 30% aromatic derivatives for crude oil-derived products. Since paraffins have higher hydrogen-to-carbon ratio than aromatics, this implies lower density and higher energy content on a weight basis for gas-to-liquids fuels compared to oil-based fuels. Due to the lower density, the volumetric energy content of gas-to-liquids products is however lower than that of oil derivatives. In addition, linear paraffins are more easily and efficiently transformed into other products than aromatics and branch paraffins.

Finally, all gas-to-liquids products are virtually sulfur-free (sulfur content: <1 ppm), since a large part of sulfur compounds is removed during the synthesis gas production step. The remaining small traces of sulfur are further separated before the gas-to-liquids synthesis, because the catalysts for GTL processing are extremely sensitive even to low contaminations of sulfur.

See also: Gasification, Synthesis Gas, Synthesis Gas Quality.

Synthesis Gas – Quality

The various technologies are (i) bubbling fluidized bed, (ii) circulating fluidized bed, and (iii) indirectly heated gasifiers.

The indirectly fired gasifiers produce the highest heating value synthesis gas ranging from 320 to 485 Btu/ft³ using air. As far as power generation using synthesis gas is concerned, the high heating value with less tar component is more important than the composition of the synthesis gas, however, for other applications such as synfuel, methanol production, and the hydrogen/carbon monoxide ratio. In general, indirectly heated gasifiers generate synthesis gas with a high percentage of hydrogen, methane, and C_{2+} compounds which directly contribute for the higher heating value of the synthesis gas. Similarly, for the directly fired gasifiers, the higher range of hydrogen, methane, and C_{2+} components correspond to the combustion using oxygen, leading to a higher calorific value of the synthesis gas. The absence of nitrogen (inert) in the system largely helps to concentrate the composition of synthesis gas with higher heating value components. Production of tars, chars, and volatile alkalis are problems associated with gasification which requires further cleaning before utilized in turbines for power generation.

The product stream at high pressure and temperature needs to be cleaned under hot conditions not lower than 540°C (1,005°F) (tar dew point) in order to maximize the energy conversion efficiency. Thus, a hot clean-up system is required, for which either catalytic tar crackers or a thermal tar cracker could be utilized. A catalytic tar reformer will operate at temperatures comparable to gasifier temperature of 825°C (1,515°F), while a thermal cracker will typically operate at 870 to 980°C (1,600 to 1,795°F). After the tar reformer/cracker, the product gas will be partially cooled to minimize the amount of alkali vapors, typically to 350–650°C. The product will then pass through a filter to remove solids. As gas turbine application limits the alkali to less than 25 ppb, much of alkali as well needs to be removed.

See also: Gasification, Synthesis Gas.

Synthetic Fuels

Gaseous or liquid synthetic fuels are obtained by converting a carbonaceous material to another form. In the United States, the most abundant naturally occurring materials suitable for this purpose are coal, tar sand, and oil shale. The

conversion of these raw materials is carried out to produce synthetic fuels to replace the depleted, unavailable, or costly supplies of natural fuels. However, the conversion may also be undertaken to remove sulfur or nitrogen that would otherwise be burned, giving rise to undesirable air pollutants. Another reason for conversion is to increase the calorific value of the original raw fuel by removing unwanted constituents such as ash, and thereby to produce a fuel which is cheaper to transport and handle.

Biomass can also be converted to synthetic fuels, and the fermentation of grain to produce alcohol is a well-known example. In the United States, grain is an expensive product which is generally thought to be more useful for its food value. Wood is an abundant and accessible source of bio-energy, but it is not known whether its use to produce synthetic fuels is economical. The procedures for the gasification of cellulosic materials have much in common with the conversion of coal to gas, and options are available for the use of the products.

Generally, the more hydrogen that is added to the raw material, the lower the boiling point of the synthesized product. Also, the more hydrogen that must be added, or alternatively the more carbon which must be removed, the lower the overall conversion efficiency in the manufacture of the synthetic fuel.

Synthetic fuels include low-, medium-, and high-calorific value gas; liquid fuels such as naphtha, kerosene, fuel oil, and clean solid fuels. Low-heat content gas is an ideal turbine fuel whose greatest utility will probably be in a gas-steam combined power cycle for the generation of electricity at the location where it is produced.

Medium Btu gas is also termed power gas or sometimes industrial gas, as well as synthesis gas. It may be used as a fuel gas, as a source of hydrogen for the direct liquefaction of coal to liquid fuels, or for the synthesis of methanol and other liquid fuels. Medium Btu gas may also be used for the production of high Btu gas, and is normally composed of more than 90% methane. Because of its high calorific value, this gas is a substitute for natural gas and is suitable for economic pipeline transport. For these reasons, it is referred to as substitute natural gas (SNG) or pipeline gas.

Gas can be manufactured by indirect hydrogenation by reacting steam with the feedstock either in the presence of air or oxygen. When air is used, the product gas will be diluted with nitrogen and its calorific value will be low in comparison with the gas manufactured using oxygen. The dilution of the product gas with nitrogen can be avoided by supplying the heat needed for the gasification from a hot material that has been heated with air, in a separate furnace, or in the gasifier itself before gasification. In all of the cases, the gas must be cleaned prior to using it as a fuel. This purification step involves the removal of the hydrogen sulfide, ammonia, and carbon dioxide, which are products of the gasification. Medium Btu gas, consisting mainly of carbon monoxide and hydrogen, can be further upgraded by altering the carbon monoxide-to-hydrogen ratio catalytically and then, in another catalytic step, converting the resulting synthesis gas mixture to methane. A high Btu gas can be produced by direct hydrogenation, termed hydrogasification, in which hydrogen is contacted with the coal.

Catalytic gasification accelerates the steam gasification of coal at relatively low temperatures and also catalyzes the upgrading and methanation reactions at the same low temperature in the same unit. Gas can also be produced by pyrolysis, that is, by the distillation of the volatile components.

Clean synthetic liquid fuels can be produced by several routes, depending on the properties and character of the feedstock. For example, in indirect liquefaction, the feedstock is first gasified, and then the liquid fuel is synthesized from the gas. This procedure is not thermally efficient, relating to the fact that the carbon bonds in the feedstock must first be broken, as in gasification, and then in a further step, some of them must be put back together again.

Another procedure is pyrolysis, the distillation of the natural oil out of the feedstock. The oil vapors are condensed, the resulting pyrolysis oil is treated with hydrogen, and the sulfur and nitrogen in it are reduced. This is similar to the procedure used in upgrading crude oil in a refinery to produce a variety of liquid fuels. Pyrolysis may also be carried out in a hydrogen atmosphere, a process termed hydrolysis, in order to increase the liquid and gas yield.

In direct liquefaction, there are two basic procedures, hydroliquefaction and solvent extraction. In the hydroliquefaction process, the feedstock is mixed with recycled oil and, together with hydrogen, fed to a high-pressure catalytic reactor where the hydrogenation of the feedstock takes place. In solvent extraction (solvent refining), the feedstock and the hydrogen are dissolved at high pressure in a recycled feedstock-derived solvent which transfers the hydrogen to the feedstock. After phase separation, the liquid product is cleaned and upgraded by refinery procedures to produce liquid fuels. In solvent refining, with a low level of hydrogen transfer, a solid, relatively clean fuel is obtained.

See also: Fuels, Gaseous Fuels, Gasification), Liquid Fuels, Synthesis Gas.

Synthetic Fuels – Production

The process of producing synfuels is often referred to as coal-to-liquids (CTL), gas-to-liquids (GTL), or biomass-to-liquids (BTL), depending on the initial feedstock.

Gas to liquids is a process for conversion of natural gas into longer-chain hydrocarbon derivatives. Thus, methane-rich gases are converted into liquid fuels either via direct conversion or via synthesis gas as an intermediate, for example using the Fischer-Tropsch process. Using such processes, refineries can convert some of their gaseous waste products into valuable fuel oils, which can be sold as or blended only with diesel fuel. The process may also be used for the economic extraction of gas deposits in locations where it is not economic to build a pipeline.

The best known synthesis process is the Fischer-Tropsch synthesis which was used on a large scale in Germany during World War II. Other processes include the Bergius process, the Mobil process, and the Karrick process. An intermediate step in the production of synthetic fuel is often synthesis gas, a stoichiometric mixture of carbon monoxide and hydrogen, which is sometimes directly used as an industrial fuel.

Several factors do make fuels from renewable sources attractive relative to conventional crude oil-based fuels. For example, the renewable source is available in quantities sufficient to meet current demand for centuries. In addition, many of the raw materials can produce naphtha or kerosene directly without the need for additional refining steps such as reforming or cracking. In some cases, there is no need to convert vehicle engines to use a different fuel and, moreover, the distribution network is already in place.

However, with higher costs of production and higher risks, companies may be well inclined to seek tax credits for the production of synthetic fuels from non-conventional sources. In allowing these credits, governments will be well advised to consider the value of a measure of energy independence.

Canada asked this question in the 1970s with respect to the development of the Athabasca oil sands (tar sands) located in north-eastern Alberta. As a result, production is now 1,000,000 bbls/day of synthetic crude oil which makes a considerable difference to the imports of non-domestic crude oil by Canada.

See also: Fuels, Gaseous Fuels, Gasification, Liquid Fuels, Synthesis Gas.

Synthetic Gas

As opposed to natural gas which is produced over geological time by the decay of organic material, synthetic gas is any gas that is produced by processes other than natural processes.

The increasing demand for natural gas and fluctuation natural gas prices in the recent past has led many to pursue unconventional methods of alternate sources of gaseous fuels. In one particular aspect of gas production, biogas from biomass is expected to become increasingly important in the future. In fact, there are two major approaches to convert biomass into gas which are (i) fluidized bed gasification with subsequent catalytic reforming, both operating around 900°C (1,650°F), and (ii) entrained flow gasification at approximately 1,300°C (2,370°F) with extensive pre-treatment.

The fluidized bed gasification of biomass approach has the advantage that the gasification technology has been developed for the production of heat and/or electricity. In addition, entrained flow gasification processes have already been developed. However, the biomass feedstock, however, needs to be pre-treated in order to take full advantage of these technologies. Pretreatment is necessary and focuses on pre-treatment such as flash pyrolysis and production of a high energy density slurry and torrefaction for the production of a suitable feedstock. Close-coupled pre-treatment options include slow pyrolysis (500°C, 930°F) and followed by choice of the gasification process.

See also: Synthetic Gas – Blue Water Gas, Synthetic Gas – Carbureted Water Gas, Synthetic Gas – Producer Gas, Synthesis Gas.

See also: Natural Gas, Methanation, Synthesis.

Synthetic Gas – Biogas

Biogas, sometimes incorrectly known as swamp gas, typically refers to a biofuel gas produced by anaerobic digestion or fermentation of organic matter including manure, sewage sludge, municipal solid waste, biodegradable waste, or

any other biodegradable feedstock, under anaerobic conditions. Depending on where it is produced, biogas is also called swamp gas, marsh gas, landfill gas, and digester gas.

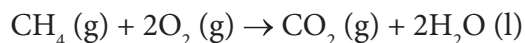
Biogas is produced by means of anaerobic digestion which is a process whereby organic matter is broken down by microbiological activity, and, as the name suggests, it is a process which takes place in the absence of air. It is a phenomenon that occurs naturally at the bottom of ponds and marshes and gives rise to marsh gas or methane, which is a combustible gas. There are two common man-made technologies for obtaining biogas; the first (which is more widespread) is the fermentation of human and/or animal waste in specially designed digesters. The second is a more recently developed technology for capturing methane from municipal waste landfill sites. The digestion of animal and human waste yields several benefits: (i) the production of methane for use as a fuel, (ii) the waste is reduced to slurry which has a high nutrient content which makes an ideal fertilizer which, in some cases, is the main product from the digester and the biogas is merely a by-product, and (iii) during the digestion process, bacteria in the manure are killed, which is a great benefit to environmental health.

In the process, the waste is fed into the digester via the inlet pipe and undergoes digestion in the digestion chamber. The temperature of the process is quite critical – methane-producing bacteria operate most efficiently at temperatures between 30 and 40°C (86 to 104°F) or 50 and 60°C (122 to 140°F), and in colder climates, heat may have to be added to the chamber to encourage the bacteria to carry out their function. The product is a combination of methane and carbon dioxide, typically in a ratio on the order of 6:4. Digestion time ranges from a couple of weeks to a couple of months depending on the feedstock and the digestion temperature. The residual slurry is removed at the outlet and can be used as a fertilizer.

The composition of biogas varies depending upon the composition of the waste material in the landfill and the anaerobic digestion process. Landfill gas typically has methane concentrations around 50%. Advanced waste treatment technologies can produce biogas with 55 to 75% v/v methane; often, air is introduced (equivalent to 5% v/v) for microbiological desulfurization. For example, the constituents of biogas generally are methane (50 to 75% v/v), carbon dioxide (25 to 50% v/v), nitrogen (0 to 10% v/v), hydrogen (0 to 1% v/v), hydrogen sulfide (0 to 3% v/v), and oxygen (0 to 2% v/v).

If biogas is cleaned by any one of a variety of relevant processes, the product gas has the same characteristics as natural gas. In this instance, the producer of the biogas can utilize the local gas distribution networks. The gas must be clean to reach pipeline quality. Water (H₂O), hydrogen sulfide (H₂S), and particulates are removed if present at high levels or if the gas is to be completely cleaned. Carbon dioxide is less frequently removed, but it must also be separated to achieve pipeline-quality gas. If the gas is to be used without extensively cleaning, it is sometimes co-fired with natural gas to improve combustion. Biogas cleaned up to pipeline quality is called *renewable natural gas*. In this form, the gas can be used in any application in which natural gas is used.

Biogas is almost identical to natural gas (methane, CH₄). The equation for the complete combustion of methane is given:



Natural gas, which is generally found associated with fossil fuels, coal, and gas hydrates (clathrates of methane in ice crystals), may also contain small amounts of ethane, propane, butane, and pentane, which are higher-boiling hydrocarbon derivatives removed prior to use as a consumer fuel, as well as carbon dioxide, nitrogen, helium, and hydrogen sulfide. Biogas is produced by methanogenic organisms in landfills, swamps, and marshes, by the decomposition of organic (both animal and plant) matter. The anaerobic (low or no oxygen present in the system) decomposition produces methane, carbon dioxide, a small amount of hydrogen, and a small amount of heat. Acidity, the carbon-to-nitrogen ratio of the feedstock, temperature, and percentage of solids all influence the quality and quantity of biogas produced. Normally, cow manure, enriched by vegetable matter, is the ideal feedstock. The other principal type of biogas is wood gas which is created by gasification of wood or other biomass. This type of biogas is comprised primarily of nitrogen, hydrogen, and carbon monoxide, with trace amounts of methane. Industrial anaerobic digesters and mechanical biological treatment systems are becoming increasingly popular. Methane is a potent greenhouse gas but is also a clean, easy burning fuel, and hence harnessing it from natural sources such as landfills is beneficial to the natural environment.

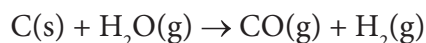
Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. In addition to biogas, there is also the possibility of using the solid by-product as a biofuel. The technologies for gas production from biomass include: (i) fermentation, (ii) gasification, and (iii) direct biophotolysis.

Synthetic Gas – Blue Water Gas

Blue water gas (also called blue gas) is a gas consisting mainly of carbon monoxide and hydrogen, made by passing steam over red-hot coke and burning with a blue flame, used especially as a source of hydrogen.

The constituents of the gas are predominantly carbon monoxide and hydrogen, formed by the action of steam upon hot coke; used mainly as a source of hydrogen and in the synthesis of other chemical compounds. The gas is used as a fuel gas used in the industrial synthesis of organic chemicals, and in welding, glassmaking, and other high-temperature industrial applications.

Water gas is made by passing steam over a bed of hot coal or coke. It mainly consists of carbon monoxide (CO) and hydrogen (H₂), contaminated with small amounts of carbon dioxide (CO₂), nitrogen (N₂), methane (CH₄), and oxygen (O₂).



See also: Synthetic Gas – Water Gas.

Synthetic Gas – Carbureted Water Gas

Carbureted water is a water gas that has been enriched by mixing the water gas hydrocarbon gases to increase the fuel value.

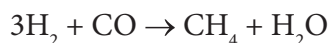
The process for manufacturing carbureted water gas consists of a single generator having a bed of solid fuel, a single carburetor, a single superheater, a regenerator containing a body of refractory and heat-accumulative material, and a gas offtake seal. The process involves air blasting the generator fuel bed, conducting the resultant gas through the carburetor and superheater, and burning it to heat the same. The gas is subsequently passed back through the superheater and carburetor and then downward through the generator fuel bed, conducting the hot back-run water gas produced through the regenerator to heat the same and cool said gas. Back-run gas is then passed through the gas offtake seal at intervals subsequent to the air-blasting and back-steaming period while passing steam through the said heated regenerator, conducting resultant uprun water gas through the heated carburetor and superheater and carbureting it during its passage through said carburetor and superheater by introducing oil.

See also: Carbureted Blue, Gas, Synthetic Gas – Water Gas.

Synthetic Gas – High Btu Gas

High Btu gas (high heat-content gas) is essentially pure methane and often referred to as synthetic natural gas or substitute natural gas (SNG). However, to qualify as substitute natural gas, a product must contain at least 95% v/v methane, giving an energy content (heat content) of synthetic natural gas on the order of 980 to 1080 Btu/ft³.

The commonly accepted approach to the synthesis of high heat-content gas is the catalytic reaction of hydrogen and carbon monoxide:



To avoid catalyst poisoning, the feed gases for this reaction must be quite pure, and, therefore, impurities in the product are rare. The large quantities of water produced are removed by condensation and recirculated as very pure

water through the gasification system. The hydrogen is usually present in slight excess to ensure that the toxic carbon monoxide is reacted; this small quantity of hydrogen will lower the heat content to a small degree.

The carbon monoxide/hydrogen reaction is somewhat inefficient as a means of producing methane because the reaction liberates large quantities of heat. In addition, the methanation catalyst is troublesome and prone to poisoning by sulfur compounds and the decomposition of metals can destroy the catalyst. Hydrogasification may be thus employed to minimize the need for methanation:

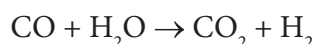
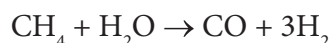


The product of hydrogasification is far from pure methane, and additional methanation is required after hydrogen sulfide and other impurities are removed.

Synthetic Gas – Hydrogen

Hydrogen is one of the basic raw materials for technological processes, including refinery processes, and will continue to play a major role for the foreseeable future (2019). In the refinery, hydrogen is produced by any one (or more) of several processes, not the least of which is the production of hydrogen from synthesis gas. Other methods, in the context of this book, include (i) steam methane reforming, (ii) biomass pyrolysis, and (iii) biomass gasification.

Steam methane reforming (SMR) is a process requiring high temperature and pressure. During the process, hydrogen is generated in reactions with methane/CO and water participation under pressure:



The process requires catalysts from nickel or nickel alloy. The gas needs to be desulfurized to prevent catalyst poisoning.

The pyrolysis of biomass, reaction, is a thermal decomposition that depends on the properties of the biomass, the use of catalysts, and the temperature: The process achieved by rapid heating of organic wastes to high temperatures 400 to 600°C (750 to 1,120°F) and pressure. The products of the process are hydrogen, carbon monoxide, methane, tar, and oils. Optimally, hemicelluloses are degraded at temperatures on the order of 250 to 350°C (480 to 660°F), cellulose at temperatures on the order of 325 to 400°C (615 to 750°F), and lignin at temperatures on the order of from 300 to 550°C (570 to 1,020°F).

Biomass gasification is the decomposition of biomass using heat and gasifying agents (such as steam). The waste biomass useful for the process should have dry matter content higher than 65%. The catalysts proposed to be used are, e.g., dolomites, alkali catalysts, and noble metals. Temperature of process depends on the properties of the feedstock. The biomass feedstock is fragmented and dried. The catalysts proposed to be used are dolomite minerals, alkali catalysts, and noble metals.

Synthetic Gas – Landfill Gas

Landfill gas (LFG, sometimes referred to as refuse gas and, under the collective group, known as biogas) is produced by the microbial decomposition of landfilled waste in an oxygen-free (anaerobic) atmosphere. This generally occurs under semi-controlled conditions in a landfill; its constituents depend on the composition and age of the waste.

Landfill gas is, in fact, a fuel gas that is a by-product of current landfilling practices and hence occurs only after municipal solid waste has been sent for disposal to a landfill site. The anaerobic digestion of the buried solid organic waste produces the landfill gas naturally, as the bacterial decomposition of the organic matter continues over time. In the long run, as the use of landfills necessarily dwindles, landfill gas will disappear as a resource. It is thus of an inherently transient nature, but will be covered here as many examples of landfill gas plants exist.

The gas is approximately 65% v/v methane and 35% v/v carbon dioxide as well as traces of other organic vapors, but the composition of the gas does vary with age and the type of waste. The odor of landfill gas is associated with trace compounds such as hydrogen sulfide (H_2S or H-SH), mercaptan derivatives (RSH), and ethylene ($\text{CH}_2=\text{CH}_2$). In addition, there are several physical conditions that affect the production (the rate of production and the volume of the gas) of the gas, namely, (i) the characteristics of the waste, which is the composition and age of the refuse, as well as (ii) environmental factors, such as the presence of oxygen in the landfill, moisture content, and temperature. Other factors can affect the migration of the gas.

Synthetic Gas – Low-Btu Gas

Low Btu gas (low heat content gas) is produced during the process by oxidation of the feedstock with air; the oxygen is not separated from the air and, as a result, the gas product invariably has a low heat-content (150 to 300 Btu/ft³). Low heat-content gas is also the usual product of *in situ* gasification of coal which is essentially used as a method for obtaining energy from coal without the necessity of mining the coal, especially if the coal cannot be mined or if mining is uneconomical.

Several important chemical reactions and a host of side reactions are involved in the manufacture of low heat-content gas under the high temperature conditions employed. Low heat-content gas contains several components, four of which are always major components present at levels of at least several percent; a fifth component, methane, is marginally a major component.

The nitrogen content of low heat-content gas ranges from somewhat less than 33% v/v to slightly more than 50% v/v and cannot be removed by any reasonable means; the presence of nitrogen at these levels makes the product gas *low heat-content* by definition. The nitrogen also strongly limits the applicability of the gas to chemical synthesis. Two other noncombustible components (water, H_2O , and carbon dioxide, CO) further lower the heating value of the gas; water can be removed by condensation and carbon dioxide by relatively straightforward chemical means.

The two major combustible components are hydrogen and carbon monoxide; the H_2/CO ratio varies from approximately 2:3 to approximately 3:2. Methane may also make an appreciable contribution to the heat content of the gas. Of the minor components, hydrogen sulfide is the most significant and the amount produced is, in fact, proportional to the sulfur content of the feed coal. Any hydrogen sulfide present must be removed by one, or more, of several procedures.

Low heat-content gas is of interest to industry as a fuel gas or even, on occasion, as a raw material from which ammonia, methanol, and other compounds may be synthesized.

Synthetic Gas – Medium Btu Gas

Medium heat-content gas (medium heat-content gas) has a heating value in the range 300 to 550 Btu/ft³, and the composition is much like that of low heat-content gas, except that there is virtually no nitrogen. The primary combustible gases in medium heat-content gas are hydrogen and carbon monoxide (Kasem, 1979). Medium heat-content gas is considerably more versatile than low heat-content gas; like low heat-content gas, medium heat-content gas may be used directly as a fuel to raise steam, or used through a combined power cycle to drive a gas turbine, with the hot exhaust gases employed to raise steam, but medium heat-content gas is especially amenable to synthesize methane (by methanation), higher hydrocarbon derivatives (by Fischer-Tropsch synthesis), methanol, and a variety of synthetic chemicals.

The reactions used to produce medium heat-content gas are the same as those employed for low heat-content gas synthesis, the major difference being the application of a nitrogen barrier (such as the use of pure oxygen) to keep diluent nitrogen out of the system.

In medium heat-content gas, the H_2/CO ratio varies from 2:3 C to 3:1 and the increased heating value correlates with higher methane and hydrogen contents as well as with lower carbon dioxide contents. Furthermore, the very nature of the gasification process used to produce the medium heat-content gas has a marked effect upon the ease of subsequent processing. For example, the CO_2 -acceptor product is quite amenable to use for methane production

because it has (i) the desired H_2/CO ratio just exceeding 3:1, (ii) an initially high methane content, and (iii) relatively low water and carbon dioxide contents. Other gases may require appreciable shift reaction and removal of large quantities of water and carbon dioxide prior to methanation.

Synthetic Gas – Producer Gas

Producer gas is mainly carbon monoxide with smaller amounts of hydrogen, methane, and variable nitrogen, obtained from partial combustion of coal or coke in air or oxygen, having a heat content of 110 to 160 Btu/ft³ (air combustion) or 400 to 500 Btu/ft³ (oxygen combustion).

Materials such as glass and metals are removed during the treatment processing since they are non-combustible. Typically, the metals are removed using a magnet and the glass using mechanical.

See also: Gasification, Refuse.

Synthetic Gas – Refuse Gas

Refuse gas (also called refuse-derived fuel gas) consists largely of combustible components of such waste, as non-recyclable plastic waste (not including polyvinyl chloride paper, cardboard, labels, and other corrugated materials). The conversion of the refuse to gas is achieved by application of a thermal process.

Landfill gas is also a refuse gas, and three processes – (i) bacterial decomposition, (ii) volatilization, and (iii) chemical reactions – form landfill gas. Most landfill gas is produced by bacterial decomposition, which occurs when organic waste is broken down by bacteria naturally present in the waste and in the soil used to cover the landfill. Organic wastes include food, garden waste, street sweepings, textiles, and wood and paper products. Bacteria decompose organic waste in four phases, and the composition of the gas changes during each phase.

Landfill gases can be created when certain wastes, particularly organic compounds, change from a liquid or a solid into a vapor (volatilization). Non-methane organic compounds in landfill gas may be the result of volatilization of certain chemicals disposed of in the landfill. Finally, chemical reactions also produce landfill gas, including the formation of landfill gas, and including the formation of non-methane organic compounds, which can be created by the reactions of certain chemicals present in waste.

See also: Landfill Gas, Refuse Gas.

Synthetic Gas – Synthesis Gas

Synthesis gas is a mixture mainly of hydrogen and carbon monoxide which is comparable in its combustion efficiency to natural gas. This reduces the emissions of sulfur, nitrogen oxides, and mercury, resulting in a much cleaner fuel. The resulting hydrogen gas can be used for electricity generation or as a transport fuel. The gasification process also facilitates capture of carbon dioxide emissions from the combustion effluent (see discussion of carbon capture and storage below).

Although synthesis gas can be used as a stand-alone fuel, the energy density of synthesis gas is approximately half that of natural gas and is therefore mostly suited for the production of transportation fuels and other chemical products. Synthesis gas is mainly used as an intermediary building block for the final production (synthesis) of various fuels such as synthetic natural gas, methanol, and synthetic crude oil fuel (dimethyl ether – synthesized naphtha and kerosene).

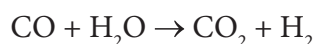
The use of synthesis gas offers the opportunity to furnish a broad range of environmentally clean fuels and chemicals, and there has been steady growth in the traditional uses of synthesis gas. Almost all hydrogen gas is manufactured from synthesis gas, and there has been an increase in the demand for this basic chemical. In fact, the major use of synthesis gas is in the manufacture of hydrogen for a growing number of purposes, especially in crude oil refineries. Methanol not only remains the second largest consumer of synthesis gas but has shown remarkable growth as part of the methyl ethers used as octane enhancers in automotive fuels.

The Fischer-Tropsch synthesis remains the third largest consumer of synthesis gas, mostly for transportation fuels but also as a growing feedstock source for the manufacture of chemicals, including polymers. The hydroformylation of olefins (the Oxo reaction), a completely chemical use of synthesis gas, is the fourth largest use of carbon monoxide and hydrogen mixtures. A direct application of synthesis gas as fuel (and eventually also for chemicals) that promises to increase is its use for *integrated gasification combined cycle* (IGCC) units for the generation of electricity (and also chemicals) from coal, crude oil coke, or high-boiling crude oil residues (particularly vacuum residues). Finally, synthesis gas is the principal source of carbon monoxide, which is used in an expanding list of carbonylation reactions, which are of major industrial interest.

Synthetic Gas – Water Gas

Water gas (carbureted blue gas) is obtained by the reaction of steam with incandescent coke. Used first as a fuel, water gas soon attracted attention as a source of hydrogen and carbon monoxide for the production of chemicals, at which time it gradually became known as synthesis gas.

The water gas process is a process by which large amounts of hydrogen gas can be generated for residential and commercial use in heating and lighting. This gas provided a more efficient heating fuel than the common coal gas, or coke gas, which was used in municipal service. The process used the water-gas shift reaction:



The process spurred on the gas manufacturing industry, and gasification plants were established quickly along the Eastern seaboard of the United States.

Synthetic Gas – Wood Gas

Wood gas is a synthetic gaseous fuel which can be used as a fuel for furnaces, stoves, and vehicles in place of gasoline, diesel fuel, or other fuels. During the production process, biomass or other renewable carbon-containing source materials are gasified within the oxygen-limited environment of a wood gas generator to produce hydrogen and carbon monoxide. These gases can then be burnt as a fuel within an oxygen-rich environment to produce carbon dioxide, water, and heat. In some gasifiers, this process is preceded by a pyrolysis step in which biomass is first converted to char, releasing methane and a tar that is rich in polycyclic aromatic hydrocarbon derivatives.

The quality of the gas from different gasifiers varies considerably. In fact, the gas composition is strongly dependent on (i) the gasification process, (ii) the gasification medium (air, oxygen, or steam), and (iii) the moisture content of the feedstock. Steam-gasification processes typically yield high hydrogen contents; downdraft fixed bed gasifiers yield high nitrogen concentrations and low tar loads, while updraft fixed bed gasifiers yield high tar load.

Staged gasifiers, where pyrolysis and gasification occur separately, instead of in the same reaction zone as was the case in, for example, the gasifiers used in the World War II period, can be engineered to produce essentially tar-free gas (less than 1 mg/m³), while the gas single-reactor fluidized bed gasifiers may exceed 50,000 mg/m³ tar. The fluidized bed reactors have the advantage of being much more compact, with more capacity per unit volume and price. Depending on the intended use of the gas, tar can be beneficial, as well by increasing the heating value of the gas.

See also: Gasification, Synthesis Gas.

Synthol Process

The Synthol process is another process that has the potential to be applied to the production of fuels from biomass.

The process has been operated at commercial scale since the 1950s by Sasol to produce synthetic fuels from coal and has undergone some evolution. The initial process, the Arge Process, involved low temperatures (200-250°C),

medium pressures, and a fixed catalyst bed. The process primarily produced a linear paraffin wax, which had use as petrochemical feedstock and also for transport fuels after further processing. This was the only process available until the 1950s/1960s when the Sasol Synthol process was developed and the process involved higher temperatures (300 to 360°C; 570 to 680°F) and medium pressures, but used a circulating fluidized bed to produce low-boiling olefins for chemicals production and naphtha components.

See also: Fischer-Tropsch Process.

Syntroleum Process

The Syntroleum process produces synthetic fuel by the Fischer-Tropsch process, which can use natural gas, coal, or biomass as feedstocks. One of the unique features of the Syntroleum process is that it uses air instead of oxygen to produce synthesis gas from natural gas in the gas-to-liquids process.

In the process, there are three major reaction steps which are (i) natural gas is first partially oxidized with air to produce synthesis gas, (ii) the synthesis gas is then reacted in a Fischer-Tropsch reactor to produce liquid hydrocarbon derivatives of various chain lengths, and (iii) the higher-boiling fraction of the products is separated and hydrocracked to transportation fuels. The liquid synthetic fuels (synfuels) produced are middle distillates consisting of naphtha, kerosene, diesel, and other hydrocarbon-based products.

See also: Fischer-Tropsch Process.

Tail Gas

Tail gas is the residual gas leaving a process, usually a Claus unit. The tail gases from the Claus units contain appreciable quantities of sulfur compounds which must be reduced before ultimate disposal of the gases to the atmosphere. The sulfur compounds in the tail gases are principally unreacted hydrogen sulfide (H_2S) and sulfur dioxide with traces of carbonyl sulfide and carbon disulfide.

The tail gas clean-up unit reduces these sulfur compounds to a level consistent with emission regulations. The Claus Unit tail gases from each train are combined, heated, and mixed with hydrogen. This mixture is then passed through a bed of cobalt-molybdenum catalyst. All of the sulfur compounds are reduced to hydrogen sulfide in this reaction.

The reactor effluent is then cooled in order to remove excess water vapor, which concentrates the hydrogen sulfide (H_2S) in the gas phase. The liquid water produced is either recycled or is fed to a sour water stripping unit. The cooled gas, now mainly nitrogen (from the Claus combustion air and the burned ammonia). Hydrogen sulfide and excess hydrogen are sweetened with very lean alkanolamine solution in a low-pressure amine absorber. The resulting sweet gas, containing only a few hundred parts per million of hydrogen sulfide, is then burned in the sulfur plant incinerator and released to the atmosphere via a tall stack. The rich alkanolamine solution is regenerated with stripping steam in a regenerator similar to the amine system regenerator. The hydrogen sulfide released is mixed with hydrogen sulfide from the main amine regenerators and is thus recycled to the Claus units as feed gas. The combination of the Claus units and the tail gas clean-up unit provides a design sulfur recovery of 99.9% w/w.

Tail gas treating is the removal of the remaining sulfur compounds from gases remaining after sulfur recovery. Tail gas from a typical Claus process, whether a conventional Claus or one of the extended versions of the process, usually contains small but varying quantities of carbonyl sulfide, carbon disulfide, hydrogen sulfide, and sulfur dioxide as well as sulfur vapor. In addition, there may be hydrogen, carbon monoxide, and carbon dioxide in the tail gas.

In order to remove the rest of the sulfur compounds from the tail gas, all of the sulfur-bearing species must first be converted to hydrogen sulfide which is then absorbed into a solvent and the clean gas vented or recycled for further processing. Examples of tail gas treating processes include the following: (i) caustic scrubbing, (ii) polyethylene glycol treatment, (iii) Selectox process, and (iv) sulfite/bisulfite tail gas treating.

See also: Claus Process, Gas Cleaning.

Tail Gas Cleaning

Tail gas cleaning (also called tail gas treating) involves the removal of the remaining sulfur compounds from gases remaining after sulfur recovery. Tail gas from a typical Claus process, whether a conventional Claus or one of the extended versions of the process, usually contains small but varying quantities of carbonyl sulfide, carbon disulfide, hydrogen sulfide, and sulfur dioxide as well as sulfur vapor. In addition, there may be hydrogen, carbon monoxide, and carbon dioxide in the tail gas. In order to remove the rest of the sulfur compounds from the tail gas, all of the sulfur-bearing species must first be converted to hydrogen sulfide which is then absorbed into a solvent and the clean gas vented or recycled for further processing.

It is necessary to develop and implement reliable and cost-effective technologies to cope with the various sales specifications and environmental requirements. In response to this trend, several new technologies are now emerging to comply with the most stringent regulations. The typical sulfur recovery efficiencies for a Claus plant is on the order of 90 to 96% w/w for a two-stage plant and 95 to 98% w/w for a three-stage plant. Most environmental agencies require the sulfur recovery efficiency to be in the range of 98.5 to 99.9+% w/w, and, as a result, the sulfur content of the Claus plant tail gas needs to be reduced further.

Moreover, a sulfur removal process must be very precise, since some gas streams may contain only a small quantity of sulfur-containing compounds that must be reduced to several orders of magnitude. Most consumers of gas require less than 4 ppm v/v in the gas – a characteristic feature of a gas stream that contains hydrogen sulfide is the presence of carbon dioxide (generally in the range of 1 to 4% v/v). In cases where the gas stream does not contain hydrogen sulfide, there may also be a relative lack of carbon dioxide.

Tail Gas Cleaning – Beavon Process

The Beavon sulfur removal process for the clean-up of Claus plant tail gas is a two-step process in which the sulfur contaminants are first catalytically hydrolyzed and/or hydrogenated to hydrogen sulfide and the hydrogen sulfide is then converted to elemental sulfur and recovered in a Stretford process unit.

In the process, which consists of two stages, the sulfur-containing compounds, such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbonyl sulfide (COS), and carbon disulfide (CS_2), are converted to sulfur in over 99.9% efficiency. In the first stage, the various sulfur compounds are either hydrogenated or hydrolyzed to give hydrogen sulfide, while in the second stage, the hydrogen sulfide is oxidized using the Stretford process to give good-quality elemental sulfur. This process can also be utilized in synthetic natural gas plants, natural gas processing, and other similar applications.

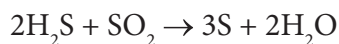
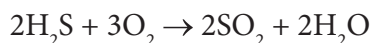
The Stretford process was developed during the late 1950s to remove hydrogen sulfide from town gas and was the first liquid phase, oxidation process for converting hydrogen sulfide to sulfur to gain widespread commercial acceptance. The process uses reduction-oxidation (redox) chemistry to oxidize the hydrogen sulfide to elemental sulfur, in an alkaline solution containing vanadium as an oxygen carrier.

See also: Stretford Process.

Tail Gas Cleaning – Claus Process

The Claus process is not so much a gas cleaning process but a process for the disposal of hydrogen sulfide, a toxic gas that originates in most gas streams. Burning hydrogen sulfide as a fuel gas component or as a flare gas component is precluded by safety and environmental considerations since one of the combustion products is the highly toxic sulfur dioxide (SO_2), which is also toxic. As described above, hydrogen sulfide is typically removed from gas streams by means of an olamine process after which application of heat regenerates the olamine and forms an acid gas stream. Following from this, the acid gas stream is treated to convert the hydrogen sulfide to elemental sulfur and water. The conversion process utilized in most modern refineries is the Claus process, or a variant thereof.

The Claus process involves the combustion of approximately one-third of the hydrogen sulfide to sulfur dioxide and then the reaction of the sulfur dioxide with the remaining hydrogen sulfide in the presence of a fixed bed of activated alumina, cobalt molybdenum catalyst resulting in the formation of elemental sulfur:



Different process flow configurations are in use to achieve the correct hydrogen sulfide/sulfur dioxide ratio in the conversion reactors.

In a split-flow configuration, one-third split of the acid gas stream is completely combusted, and the combustion products are then combined with the non-combusted acid gas upstream of the conversion reactors. In a once-through configuration, the acid gas stream is partially combusted by only providing sufficient oxygen in the combustion chamber to combust one-third of the acid gas.

Two or three conversion reactors may be required depending on the level of hydrogen sulfide conversion required. Each additional stage provides incrementally less conversion than the previous stage. Overall, conversion of 96 to

97% v/v of the hydrogen sulfide to elemental sulfur is achievable in a Claus process. If this is insufficient to meet air quality regulations, a Claus process tail gas treater is utilized to remove essentially the entire remaining hydrogen sulfide in the tail gas from the Claus unit. The tail gas treater may employ a proprietary solution to absorb the hydrogen sulfide followed by conversion to elemental sulfur.

See: Gas Cleaning, Tail Gas, Tail Gas Cleaning – SCOT Process.

Tail Gas Cleaning – SCOT Process

The SCOT (Shell Claus Off-gas Treating) unit is a most common type of tail gas unit and uses a hydrotreating reactor followed by amine scrubbing to recover and recycle sulfur, in the form of hydrogen, to the Claus unit.

Early SCOT units used diisopropanolamine in the Sulfinol (Sulfinol-D) solution. Methyl diethanolamine-based Sulfinol (Sulfinol-M) was used later to enhance hydrogen sulfide removal and to allow for selective rejection of carbon dioxide in the absorber. To achieve the lowest possible hydrogen sulfide content in the treated gas, the Super-SCOT configuration was introduced. In this version, the loaded Sulfinol-M solution is regenerated in two stages. The partially stripped solvent goes to the middle of the absorber, while the fully stripped solvent goes to the top of the absorber. The solvent going to the top of the absorber is cooled below that used in the conventional SCOT process.

In the process, tail gas (containing hydrogen sulfide and sulfur dioxide) is contacted with hydrogen and reduced in a hydrotreating reactor to form hydrogen sulfide and water. The catalyst is typically cobalt/molybdenum on alumina. The gas is then cooled in a water contractor. The hydrogen sulfide-containing gas enters an amine absorber which is typically in a system segregated from the other refinery amine systems. The purpose of segregation is twofold: (i) the tail gas treater frequently uses a different amine than the rest of the plant, and (ii) the tail gas is frequently cleaner than the refinery fuel gas (in regard to contaminants) and segregation of the systems reduces maintenance requirements for the SCOT unit. Amines chosen for use in the tail gas system tend to be more selective for hydrogen sulfide and are not affected by the high levels of carbon dioxide in the off-gas.

However, the SCOT process can be configured in various ways. For example, it can be integrated with the upstream acid gas removal unit if the same solvent is used in both units. Another configuration has been used to cascade the upstream gas clean-up with the SCOT unit. A hydrogen sulfide-lean acid gas from the upstream gas treating unit is sent to a SCOT process with two absorbers. In the first absorber, the hydrogen sulfide-lean acid gas is enriched, while the second absorber treats the Claus tail gas. A common stripper is used for both SCOT absorbers, and, in this latter configuration, different solvents could be used in both the upstream and the SCOT units.

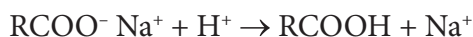
A hydrotreating reactor converts sulfur dioxide in the off-gas to hydrogen sulfide that is then contacted with a Stretford solution (a mixture of a vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide) in a liquid-gas absorber. The hydrogen sulfide reacts stepwise with sodium carbonate and the anthraquinone sulfonic acid to produce elemental sulfur, with vanadium serving as a catalyst. The solution proceeds to a tank where oxygen is added to regenerate the reactants. One or more froth or slurry tanks are used to skim the product sulfur from the solution, which is recirculated to the absorber. Other tail gas treating processes include: (i) caustic scrubbing, (ii) polyethylene glycol treatment, (iii) Selectox process, and (iv) a sulfite/bisulfite tail gas treating.

See also: Gas Cleaning, Tail Gas, Tail Gas Cleaning – Claus Process.

Tall Oil

Tall oil is an important by-product separated from the black liquor by skimming before the liquor is sent to the evaporators or after the first evaporator stage. It is a mixture of mainly acidic compounds found, like turpentine, in pine trees and obtained as a by-product of the pulp and paper industry. Tall oil is a dark, viscous, and odorous liquid that phase-separates from the used pulping liquor (alkaline black liquor) that remains after the pulping of wood chips, and contains sodium soaps of rosin and fatty acids. It is extracted at the pulp and paper mill, and undergoes the first two processing steps there.

In the first step, the black liquor from the paper making process is concentrated and left to settle. The top layer is known as “tall oil soap,” and is skimmed off. The rest is recycled for further use in paper making. In the second step, the tall oil soap is reacted with acid to form crude tall oil. The following reaction occurs:



The acids formed from this reaction, along with small quantities of other compounds of similar volatility, make up the crude tall oil. All crude tall oil produced in New Zealand is then sent to a plant in Mt. Maunganui to complete processing.

In the third step, the crude tall oil is distilled into five components with different boiling points: overhead fractions (which boil first), then fatty acids, distilled tall oil (a mixture of fatty and resin acids), resin acids (collectively known as rosin), and pitch (the residue). All of these can be used in various industries as is, but some of the rosin is also further processed on site.

The major processing feature of the distillation is that the tall oil and its products are sensitive to heat. Excessive temperature or holding at temperature for long periods of time will cause degradation and subsequent loss of product, or at least a discolored product. This is countered by the use of high vacuum for all the distillation columns and thin film wiped evaporators as the reboilers. These measures minimize the operating temperatures experienced by the fluids and the time to which they are exposed to heat. The high vacuum operation also helps in the distillation by exaggerating the relative volatility differences between the components, while also minimizing the thermal energy requirements of the process. The net result of the distillation process is the production of three main products: fatty acids, distilled tall oil, and rosin, plus some quantities of residue (pitch) and an overhead stream.

There is a reasonable market for the fatty acids and distilled tall oil but a poor market for rosin. The main value of rosin is that it can be used to manufacture rosin size and a variety of other specialty substances such as rosin oils and tackifiers. In preparation of those rosin-based products, proportions of distilled tall oil and pitch can also be utilized to maximize the saleable product recovered from the crude tall oil. Any pitch which cannot be incorporated into saleable products can be used as a fuel in the tall oil plant itself.

Tall oil itself has a variety of uses in industry. It is used as a resin in many different industries, including mining, paper manufacture, paint manufacture, and synthetic rubber manufacture. Tall oil is also used as a frothing agent in the flotation process for reclaiming low-grade copper-, lead- and zinc-bearing ores, and as a solvent or wetting agent in a variety of textile and synthetic fiber manufacturing processes. The distilled fatty acids are used in soaps, detergents, and disinfectants and as a base for lubricating greases, textile oils, cutting oils, and metal polishes. They are also used as drying agents in paint, although synthetic substances are becoming widely used. The fatty acids are unsaturated and on exposure to air undergo autoxidation and polymerization to form resin-like materials which form a tough protective coating.

Resin acids are used in rubber polymerization and compounding, as size to impart water resistance to paper (see below), and in adhesives and printing inks. Resin acids are the major component of a substance known as rosin, which is used by musicians to improve the grip of bows used for string instruments. One of the common sterols found in the unsaponifiable portion of tall oil is ergosterol, a compound which forms a number of products, including vitamin D2 (calciferol), on irradiation with ultraviolet light. If a suitable process to carry out this reaction commercially is found, then the unsaponifiable fraction of tall oil may also have a use in the future.

See also: Black Oil, Fish Oil.

Tallow

Tallow is a rendered form of animal fat. More specifically, tallow is rendered mutton, beef, or other bovine fat, processed from suet. Rendered fat obtained from pigs is known as lard. From its early use in lamps, tallow is now being considered as a source of biodiesel.

Tallow is solid at room temperature, and pure tallow is a creamy-white substance. Unlike suet, tallow can be stored for extended periods without the need for refrigeration to prevent decomposition, provided it is kept in an airtight container to prevent oxidation.

The rendering process evaporates the moisture and enables the fat, known as tallow, to be separated from the high-protein solids, known as greaves. The greaves are pressed, centrifuged, or subjected to a process of solvent extraction to remove more tallow, before being ground into meat and bone meal. The viscosity of tallow can be significantly reduced by esterification, and blends of the esterified product yield a fuel with properties similar to the properties of No. 2 diesel fuel. Biodiesel from tallow has a higher cetane number than plant oil biodiesel. This means cleaner and more efficient burning in diesel engines.

Cetane numbers rate the ignition properties of diesel fuels, just as octane numbers determine the quality and value of petrol. It is a measure of ability of the fuel to ignite when it is compressed – the higher the cetane number, the more efficient the fuel.

Biodiesel has a higher cetane number than petrodiesel because of its oxygen content. The ignition quality affects engine performance, cold starting, warm up, and engine combustion roughness. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion.

Biodiesel made from tallow has a higher cloud point than conventional diesel derived from crude oil. Because of the high levels of saturates, biodiesel from tallow tends to crystallize out at much higher temperatures than biodiesel from plant oils. In northern climates, this makes tallow biodiesel unsuitable for winter use apart from blending at low rates into conventional diesel.

See also: Biodiesel.

Tar Removal from Gas Streams

Tar is a highly viscous liquid product (typically produced in thermal processes) that condenses in the low temperature zones of the equipment (the pyrolyzer or the gasifier), thereby interfering with the gas flow and leading to system disruption. It is, perhaps, the most undesirable product of the process, and high residual tar concentrations in the can gas prevent utilization.

Biomass is considered an important source of renewable energy needed to realize renewable energy goals and goals for the reduction of carbon dioxide emissions. Biomass gasification as a technology is recognized generally as highly desirable because of its high efficiency toward all kind of energy products. Biomass can be gasified using many different technologies ranging from high-temperature processes as high as 1,500°C (2,730°F) to low-temperature processes as low as 500°C (930°F), compared to gasifiers operated at 800 to 900°C. In many cases, the gasification process is accompanied by the formation of tar. Thus, the technical obstacle of biomass gasification technology is the effective removal of tar, which will cause the clogging of pipes and engines. In most cases, a bio-oil scrubber and the char bed are effective for tar removal.

Methods for reduction or elimination of tar can be divided into two broad groups: (i) in situ tar reduction, also called primary tar reduction, which focuses on reducing or avoiding tar formation in the reactor, and (ii) post-gasification tar reduction, also called secondary tar reduction, which strips the tar from the product gas. A combination of in situ and post-gasification tar reductions can prove to be more effective than either of the single stages alone. The two basic post-gasification methods are physical removal and cracking (catalytic or thermal).

See also: Gas Cleaning.

Tar Removal from Gas Streams – Physical Methods

In a process for the physical removal of tar, the tar is treated tar as dust particles or mist and the tar is condensed before separation. Physical tar removal can be accomplished by cyclones, barrier filters, wet electrostatic precipitators (ESPs), or wet scrubbers. The selection of the equipment application depends on the load concentrations of particulate matter (PM) and tar, particle size distribution, and particulate tolerance of downstream users.

Cyclone collectors are the most common of the inertial collector class and are effective in removing coarser fractions of particulate matter and operate by contacting the particles in the gas stream with a liquid. In principle, the particles are incorporated in a liquid bath or in liquid particles which are much larger and therefore more easily collected. In the process, the particle-laden gas stream enters an upper cylindrical section tangentially and proceeds

downward through a conical section. Particles migrate by centrifugal force generated by providing a path for the carrier gas to be subjected to a vortex-like spin. The particles are forced to the wall and are removed through a seal at the apex of the inverted cone. A reverse-direction vortex moves upward through the cyclone and discharges through a top center opening. Cyclones are often used as primary collectors because of their relatively low efficiency (50 to 90% is usual). Cyclones may not be efficient when removing small tar droplets, and barrier filters are porous material which can capture a certain amount of tar when the product gas passes through the filters. As an aid, catalyst grains can be integrated as a fixed bed inside the filter to promote the simultaneous removal of particulate matter and tar.

Fabric filters are typically designed with non-disposable filter bags. As the gaseous (dust-containing) emissions flow through the filter media (typically cotton, polypropylene, fiberglass, or Teflon), particulate matter is collected on the bag surface as a dust cake. Fabric filters operate with collection efficiencies up to 99.9% although other advantages are evident, but there are several issues that arise during use of such equipment.

Wet scrubbers are devices in which a countercurrent spray liquid is used to remove particles from an air stream. Device configurations include plate scrubbers, packed bed scrubbers, orifice scrubbers, venturi scrubbers, and spray towers, individually or in various combinations. Wet scrubbers can achieve high collection efficiencies at the expense of prohibitive pressure drops. The *foam scrubber* is a modification of a wet scrubber in which the particle-laden gas is passed through a foam generator, where the gas and particles are enclosed by small bubbles of foam.

Electrostatic precipitators operate on the principle of imparting an electric charge to particles in the incoming air stream, which are then collected on an oppositely charged plate across a high-voltage field. Particles of high resistivity create the most difficulty in collection. Conditioning agents such as sulfur trioxide (SO_3) have been used to lower resistivity. Important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include the use of high-voltage pulse energy to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations. Wet electrostatic precipitator units have a high collection efficiency (on the order of 90%) over the entire range of particle size down to 0.5 μm with a very low-pressure drop. Wet scrubbers can achieve a high collection efficiency (also on the order of 90%).

Other methods include use of high-energy input *venturi scrubbers* or electrostatic scrubbers where particles or water droplets are charged, and flux force/condensation scrubbers where a hot humid gas is contacted with cooled liquid or where steam is injected into saturated gas. In the latter scrubber, the movement of water vapor toward the cold water surface carries the particles with it (*diffusiophoresis*), while the condensation of water vapor on the particles causes the particle size to increase, thus facilitating collection of fine particles.

See also: Gas Cleaning.

Tar Removal from Gas Streams – Thermal Methods

Cracking methods are more advantageous in terms of recovering the energy content in the tar by converting the high-molecular-weight constituents of the tar into lower-molecular-weight (gaseous) products such as hydrocarbon derivatives and hydrogen at high temperature (up to 1,200°C, 2,190°F) or catalytic reactions (up to 800°C, 1,470°F). Catalytic cracking is commercially used in many refineries plants and has been demonstrated to be one of the most effective processes for the conversion of high-molecular-weight products (such as crude oil residua, heavy oil, extra heavy oil, and tar sand bitumen) into gases and lower-molecular-weight distillable and liquids.

Non-metallic catalysts such as dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), calcite (CaCO_3), zeolite, and metallic catalysts such as nickel-based catalysts, nickel/molybdenum-based catalysts, nickel/cobalt-based catalysts, molybdenum-based catalysts, platinum-based catalysts, and ruthenium-based catalysts Mo, NiO, Pt, and Ru have been applied to various tar conversion processes.

Tar removal can also be achieved by catalytic reforming which has the advantage of keeping the carbon contained in the tars available for further conversion to fuel. Another option to reduce the tar content of the synthesis gas is the use of catalytic bed material in the gasification reactor. Olivine sand has been shown to effectively reduce the tar content in a gas stream from steam gasification.

See also: Gas Cleaning.

Tar Sand

Tar sand (also referred to as oil sand) is a combination of clay, sand, water, and bitumen, a heavy black viscous material that resembles petroleum residua. Tar sand can be mined and processed to extract the oil-rich bitumen, which is then refined into oil. The bitumen in tar sand cannot be pumped from the ground in its natural state. Instead, tar sand deposits are mined, usually using strip mining or open pit techniques, or the oil is extracted by underground heating with additional upgrading.

Tar sand have been defined in the United States (FE-76-4) as:

...the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques. The hydrocarbon-bearing rocks are variously known as bitumen-rocks oil, impregnated rocks, oil sands, and rock asphalt.

By inference, heavy oil can be recovered in its natural state by enhanced oil recovery techniques while conventional crude oil can be recovered in its natural state by secondary and primary recovery techniques. Also by inference, black oil does not reliably fit into this definition.

To recover bitumen from tar sand recovery processes involves extraction and separation systems to separate the bitumen from the clay, sand, and water that make up the tar sand. Bitumen also requires additional upgrading before it can be refined. Because it is so viscous (thick), it also requires dilution with lighter hydrocarbons to make it transportable by pipelines.

Resources

Much of the potential oil of the world (more than 2 trillion barrels, 2×10^{12} barrels) is in the form of tar sand, although it is not all recoverable. While tar sand deposits are found in many places worldwide, the largest deposits in the world are found in Canada (Alberta) and Venezuela, and much of the rest is found in various countries in the Middle East. In the United States, tar sand resources are primarily concentrated in Eastern Utah, mostly on public lands.

The Industry

Currently, synthetic crude oil is not produced from tar sand on a significant commercial level in the United States; in fact, only Canada has a large-scale commercial tar sand industry, though a small amount of oil from tar sand is produced commercially in Venezuela. The Canadian tar sand industry is centered in Alberta, and more than one million barrels of synthetic oil are produced from these resources per day. Currently, synthetic crude oil from tar sand deposits represents approximately 40% of Canada's oil production, and the output is expanding rapidly. Approximately 20% of U.S. crude oil and products come from Canada, and a substantial portion of this amount comes from tar sand. The bitumen from tar sand is extracted both by mining and *in situ* recovery methods.

Bitumen Extraction and Processing

Thermal recovery methods have found most use when tar sand bitumen has an extremely high viscosity under reservoir conditions. For example, tar sand bitumen is highly viscous, with a viscosity ranging from a thousand centipoises to a million centipoises or more at the reservoir conditions. In addition, oil viscosity is also a function of temperature and API gravity.

Thermal enhanced oil recovery processes (i.e., cyclic steam injection, steam flooding, and in situ combustion) add heat to the reservoir to reduce oil viscosity and/or to vaporize the oil. In both instances, the oil is made more mobile so that it can be more effectively driven to producing wells. In addition to adding heat, these processes provide a driving force (pressure) to move oil to producing wells. In situ combustion may make a comeback with a new concept. THAI (toe-to-heel air injection) is based on the geometry of horizontal wells that may solve the problems that have plagued conventional in situ combustion.

In situ conversion, or underground refining, is a promising new technology to tap the extensive reservoirs of heavy oil and deposits of bitumen. The new technology (Gregoli and Rimmer, 2000; Gregoli et al., 2000) features the injection of high-temperature, high-quality steam and hot hydrogen are into a formation containing heavy hydrocarbons to initiate conversion of the heavy hydrocarbons into lighter hydrocarbons. In effect, the heavy hydrocarbons

undergo partial underground refining that converts them into a synthetic crude oil (or *syncrude*). The heavier portion of the syncrude is treated to provide the fuel and hydrogen required by the process, and the lighter portion is marketed as a conventional crude oil.

Thus, below ground, superheated steam and hot hydrogen are injected into a tar sand formation, which simultaneously produces the bitumen and converts it *in situ* (i.e., within the formation) into syncrude. Above ground, the heavier fraction of the syncrude is separated and treated on-site to produce the fuel and hydrogen required by the process, while the lighter fraction is sent to a conventional refinery to be made into petroleum products.

The potential advantages of an *in situ* process for tar sand bitumen include (i) leaving the carbon forming precursors in the ground, (ii) leaving the heavy metals in the ground, (iii) reducing the sand handling, and (iv) bringing a partially upgraded product to the surface. The extent of the upgrading can, hopefully, be adjusted by adjusting the exposure of the bitumen of heavy oil to the underground thermal effects.

In the *modified in situ extraction* processes, combinations of *in situ* and mining techniques are used to access the reservoir. A portion of the reservoir rock must be removed to enable application of the *in situ* extraction technology. The most common method is to enter the reservoir through a large-diameter vertical shaft, excavate horizontal drifts from the bottom of the shaft, and drill injection and production wells horizontally from the drifts. Thermal extraction processes are then applied through the wells. When the horizontal wells are drilled at or near the base of the tar sand reservoir, the injected heat rises from the injection wells through the reservoir, and drainage of produced fluids to the production wells is assisted by gravity.

Generally, tar sand bitumen recovery requires a higher degree of thermal stimulation because bitumen, in its immobile state, is extremely difficult to move to a production well. Extreme processes are required, usually in the form of a degree of thermal conversion that produces free-flowing product oil that will flow to the well and reduce the resistance of the bitumen to flow.

The mining method of bitumen recovery has received considerable attention since it was chosen as the technique of preference for the only two commercial bitumen recovery plants in operation in North America. *In situ* processes have been tested many times in the United States, Canada, and other parts of the world and are ready for commercialization. There are also conceptual schemes that are a combination of both mining (above-ground recovery) and *in situ* (non-mining recovery) methods.

Engineering a successful oil mining project must address a number of items because there must be sufficient recoverable resources, the project must be conducted safely, and the project should be engineered to maximize recovery within economic limits. The use of a reliable screening technique is necessary to locate viable candidates. Once the candidate is defined, this should be followed by an exhaustive literature search covering the local geology, drilling, production, completion, and secondary and tertiary recovery operations.

The reservoir properties, which can affect the efficiency of bitumen production by mining technology, can be grouped into three classes: (i) the primary properties, which are the properties that have an influence on the fluid flow and fluid storage properties and include rock and fluid properties, such as porosity, permeability, wettability, crude oil viscosity, and pour point, (ii) the secondary properties, which are the properties that significantly influence the primary properties, including pore size distribution, clay type, and content, and (iii) the tertiary properties, which are the properties that mainly influence oil production operation (fracture breakdown pressure, hardness, and thermal properties) and the mining operations (e.g., temperature, subsidence potential, and fault distribution).

There are also important rock mechanical parameters of the formation in which a tunnel is to be mined and from where all oil mining operations will be conducted. These properties are mostly related to the mining aspects of the operations, and not all are of equal importance in their influence on the mining technology. Their relative importance also depends on the individual reservoir.

Many of the candidate reservoirs for application of improved oil mining are those with high oil saturation resulting from the adverse effects of reservoir heterogeneity. Faulting, fracturing, and barriers to fluid flow are features that cause production of shallow reservoirs by conventional methods to be inefficient. Production of heterogeneous reservoirs by underground oil production methods requires consideration of the manner in which fractures alter the flow of fluids.

After mining, the tar sand is transported to an extraction plant, where a hot water process separates the bitumen from sand, water, and minerals. The separation takes place in separation cells. Hot water is added to the sand, and the resulting slurry is piped to the extraction plant where it is agitated.

The hot water process is, to date, the only successful commercial process to be applied to bitumen recovery from mined tar sands in North America. The process utilizes the linear and the nonlinear variation of bitumen density and water density, respectively, with temperature so that the bitumen that is heavier than water at room temperature becomes lighter than water at 80°C (180°F). Surface-active materials in the tar sand also contribute to the process. The essentials of the hot-water process involve a conditioning, separation, and scavenging.

Thus, in the hot water extraction process, the tar sand feed is introduced into a *conditioning* drum. In this step, the oil sand is heated, mixed with water, and agglomeration of the oil particles begins. The conditioning is carried out in a slowly rotating drum that contains a steam-sparging system for temperature control as well as mixing devices to assist in lump size reduction and a size ejector at the outlet end. The oil sand lumps are reduced in size by ablation and mixing action. The conditioned *pulp* has the following characteristics: (i) solids 60 to 85%; and (ii) pH 7.5 to 8.5.

In the conditioning step, also referred to as mixing or pulping, tar-sand feed is heated and mixed with water to form a pulp of 60% by weight to 85% by weight solids at 80°C to 90°C (175°F to 196°F). First, the lumps of tar sand as-mined are reduced in size by ablation, i.e., successive layers of lump are warmed and sloughed off revealing cooler layers. The conditioned pulp is screened through a double-layer vibrating screen. Water is then added to the screened material (to achieve more beneficial pumping conditions), and the pulp enters the separation cell through a central feed well and distributor. The bulk of the sand settles in the cell and is removed from the bottom as tailing, but the majority of the bitumen floats to the surface and is removed as froth. A middlings stream (mostly of water with suspended fines and some bitumen) is withdrawn from approximately midway up the side of the cell wall. Part of the middlings is recycled to dilute the conditioning drum effluent for pumping. Clays do not settle readily and generally accumulate in the middlings layer. High concentrations of clays increase the viscosity and can prevent normal operation in the separation cell. Thus, it is necessary to withdraw a drag stream to act as a purge; this is usually done at high clay concentrations but may not be as essential with a low-clay oil sand charge.

Both mining and processing of tar sand involve a variety of environmental impacts, such as global warming and greenhouse gas emissions, disturbance of mined land, and impacts on wildlife and air and water quality. The development of a commercial tar sand industry in the United States would also have significant social and economic impacts on local communities. Of special concern in the relatively arid western United States is the large amount of water required for tar sand processing; currently, tar sand extraction and processing require several barrels of water for each barrel of oil produced, though some of the water can be recycled.

A variant of tar sand bitumen – referred to as extra heavy crude oil and which has mobility because of the high temperature of the deposit – is found predominantly in Venezuela. In relation to the bitumen in the Alberta tar sand deposits, approximately 15 to 20% v/v of the bitumen is recoverable, which amounts to approximately 75% v/v of the crude oil reserves in North America. Furthermore, it is only recently that the deposits of tar sand have been recognized as viable energy sources, and there have been changes in the way the world views oil reserves, and tar sand reserves have come to be included in the tally of global crude oil and heavy crude oil reserves.

In spite of the high estimations of the reserves of bitumen, the two conditions of vital concern for the economic development of tar-sand deposits are the concentration of the resource, or the percent bitumen saturation, and its accessibility, usually measured by the overburden thickness. Recovery methods are based either on mining combined with some further processing or operation on the oil sands *in situ*. The mining methods are applicable to shallow deposits, characterized by an overburden ratio (i.e., overburden depth to thickness of tar-sand deposit) that is deposit specific. For example, indications are that for the Athabasca deposit, no more than 15 to 20% v/v of the in-place deposit is available within current concepts of the economics and technology of open-pit mining and advanced non-mining recovery techniques.

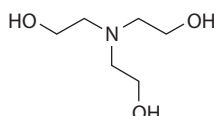
See also: Extra Heavy Crude Oil.

TEA

Ethanolamine derivatives became available commercially in the early 1930s; they assumed steadily growing commercial importance as intermediates after 1945, because of the large-scale production of ethylene oxide. Since the mid-1970s, economical production of very pure, colorless ethanolamines has been possible. Ethanolamine derivatives are produced on an industrial scale exclusively by reaction of ethylene oxide and excess ammonia. This reaction takes place slowly, but is accelerated by water. An anhydrous procedure uses a fixed-bed ion-exchange resin catalyst.

Acid gas removal is an important process in various branches of the hydrocarbon processing industry, primarily in natural gas processing and refining. Acid gas removal is also an essential part of other processes, such as coal gasification where carbon dioxide, hydrogen sulfide, carbonyl sulfide, mercaptan derivatives, and other contaminants need to be removed. Acid gas is defined as gas containing significant amounts of contaminants, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), and other acidic gases. Sour gas is gas contaminated with hydrogen sulfide, and, thus, gas sweetening refers to hydrogen sulfide removal, because it improves the odor of the gas being processed, while the term acid gas removal refers to the removal of both hydrogen sulfide and carbon dioxide. Acid gases need to be removed in order to comply with sales gas quality regulations. One such treatment for acid gas removal involves the use of ethanolamine derivatives, especially triethanolamine (TEA).

Triethanolamine (TEA) is an organic chemical compound which is both a tertiary amine and a tri-alcohol (i.e., the molecule contains three hydroxyl groups).



Like other amines, triethanolamine acts as a weak base due to the lone pair of electrons located on the nitrogen atom. See also: Gas Cleaning, Oamine Processes.

Tertiary Biomass Feedstocks

Tertiary biomass feedstock includes post-consumer residues and wastes, such as fats, greases, oils, construction and demolition wood debris, other waste wood from the urban environments, as well as packaging wastes, municipal solid wastes, and landfill gases. A category other wood waste from the urban environment includes trimmings from urban trees, which technically fits the definition of primary biomass. However, because this material is normally handled as a waste stream along with other post-consumer wastes from urban environments (and included in those statistics), it makes the most sense to consider it to be part of the tertiary biomass stream.

Tertiary biomass includes post-consumer residues and wastes, such as fats, greases, oils, construction and demolition wood debris, other waste wood from the urban environments, as well as packaging wastes, municipal solid wastes, and landfill gases.

The category “other wood waste from the urban environment” could include trimmings from urban trees, which technically fits the definition of primary biomass. However, because this material is normally handled as a waste stream along with other post-consumer wastes from urban environments (and included in those statistics), it makes the most sense to consider it to be part of the tertiary biomass stream.

The proper categorization of fats and greases may be debatable since those are by-products of the reduction of animal biomass into component parts. However, since animals can be considered to be a type of biomass processing factory and since most fats and greases, and some oils, are not available for bioenergy use until after they become a post-consumer waste stream, it seems appropriate for them to be included in the tertiary biomass category. Vegetable oils derived from processing of plant components and used directly for bioenergy (e.g., soybean oil used in biodiesel) would be a secondary biomass resource, though the amounts being used for bioenergy are most likely to be tracked together with fats, greases, and waste oils.

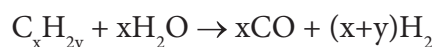
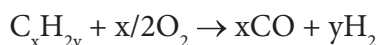
See also: Biomass, Primary Biomass Feedstocks, Secondary Biomass Feedstocks.

Texaco Gasification Process

The Texaco process is used to gasify coal under high pressure in an entrained bed by the injection of oxygen (or air) and steam with concurrent gas/solid flow. The process uses the entrained bed technology and is basically used to manufacture synthesis gas.

In the process, the feedstock, together with the feedstock carbon slurry recovered in the carbon recovery section, is pressurized to a given pressure, mixed with high-pressure steam, and then blown into the gas generator through the burner together with oxygen.

The gasification reaction is a partial oxidation of hydrocarbons to carbon monoxide and hydrogen:



The gasification reaction is instantly completed, thus producing gas mainly consisting of H_2 and CO ($\text{H}_2 + \text{CO} = >90\%$). The high-temperature gas leaving the reaction chamber of the gas generator enters the quenching chamber linked to the bottom of the gas generator and is quenched to 200 to 260°C (390 to 500°F) with water.

The coal is crushed in a two-stage system (the second step performed under an inert atmosphere) and is then mixed with water or oil to form a pumpable slurry which is pumped under pressure into the gasifier vessel (a refractory-lined chamber inside a pressure vessel). In this unit, the slurry reacts with either air or oxygen at high temperature; the product gas from the reactor contains primarily carbon monoxide and hydrogen, but may contain appreciable quantities of nitrogen if the reactor is air-blown.

Oils or tars are not usually produced by the process, and methane is the only hydrocarbon gas generated.

The product gases and molten slag produced in the reaction zone pass downward through a water spray chamber and a slag quench bath, and the cooled gas and slag are then removed for further treatment.

The gas leaving the quench unit, once it is separated from the slag, is treated to remove the carbon fines and ash. The gas is then subsequently recycled to the slurry preparation system and treated for acid gas removal; elemental sulfur is recovered from the hydrogen sulfide-rich stream.

The partial oxidation unit is also used to gasify crude oil residua and can be adjusted so that the effluent gas stream has little, or no, hydrocarbon content.

See also: Gasification.

Texaco Gasifier

Gasification has been used commercially around the world for more than a century by the chemical, refining, and fertilizer industries and for more than 35 years by the electric-power industry.

Gasification technologies can also be used to convert combined feedstocks, such as coal and biomass, in the same gasifier at the same time. Thermochemical conversion would use nonfood biomass feedstocks – such as lignin, cellulose, and plastic wastes – and thus would not raise issues of competition between the markets for fuel and food.

The Texaco gasifier is an entrained-flow, high-pressure, and high-temperature slagging system that is based on a commercially proven crude oil gasifier. Although developed for coal gasification, this type of (entrained-flow) gasifier lends itself to the gasification of dry lignocellulosic biomass. The process is compatible with biomass feedstocks from agriculture, mainly straw, which have a higher ash, potassium, and chlorine content and a lower ash softening point than wood.

The first step is a fast pyrolysis at atmospheric pressure, which produces much condensate and only little char and gas. Pyrolysis condensate and pulverized pyrolysis char are then mixed to a slurry, containing up to 90% of the initial biomass energy. In contrast to the loose-packed original biomass, the dense slurries are easily pumped and stored in tanks. From a number of regional pyrolysis plants, the slurries can be transported by rail to a large central gasification facility. The slurries are pumped into a slagging entrained flow gasifier and are atomized and converted to syngas at high operating temperatures and pressures, above the operating pressure of a downstream synthesis plant.

At high pressures, alternative operation of pressure locks with a low-bulk density biomass will become too expensive. High gasification temperatures and pressures help to produce a tar-free syngas, simplify downstream gas cleaning steps, and obviate intermediate compression before synthesis. To achieve high process efficiency, the utilization of chemical energy in synthesis products like methanol must be complemented by the use of sensible heat for electric power generation.

The economy of scale can make possible an efficient but more complex gasification and syngas utilization technology, to produce the most valuable products.

See also: Gasification.

Thermal Conversion

Thermal conversion (sometimes referred to as thermochemical conversion) involves either the gasification of biomass or coal followed by synthesis to liquid fuels (indirect liquefaction) or the direct conversion of coal to liquid fuels (direct liquefaction) with high-pressure hydrogen (H_2).

Those thermochemical conversion processes are considered to be ready for deployment between now and 2020. Because of its chemical complexity, biomass can also be converted to liquid fuels by pyrolysis or liquefaction, but these routes are not as well developed.

Thermal processes include pyrolysis, gasification, and combustion. Pyrolysis normally proceeds at temperatures below approximately 600°C (1,110°F), while in gasification processes, temperatures range from 800 to 1,100°C (1,470 to 2,110°F) or even higher in slagging systems, and combustion temperatures are 1,500°C (2,730°F) or more.

Pyrolysis occurs in the absence of oxygen, and other chemical reactants are usually not used. The products of pyrolysis are gases, liquids, and a carbonaceous char, in relative amounts dependent on the properties of the biomass, the rate of heating, and the final temperature attained. Slow pyrolysis produces mainly char, while with rapid pyrolysis, the liquid and gaseous yields are increased. Pyrolysis in a hydrogen atmosphere (hydropyrolysis) also increases the gaseous yield relative to char, and generally produces a high quantity and quality of liquid product.

In the case of gasification, one or more reactants, such as oxygen, steam, or hydrogen, are introduced into the system. These chemical reactants combine with solid carbon at the higher gasification temperatures, so increasing the gas yield while consuming char. The amount of char by-product remaining on gasification is in fact essentially zero with biomass materials, while the small quantity of tars and oils evolved may be recycled to extinction. The introduced reactants also enter into gas phase reactions which, together with the shift in equilibrium and the change in relative reaction rates at the higher temperatures, results in a significantly better-quality gas than that obtained on pyrolysis. Important distinctions between pyrolysis and gasification are therefore the improved gas yield and the elimination of solid and liquid by-products. These advantages are gained at the cost of a more complex process.

Gasification results in only a partial oxidation of the carbon constituent. Much of the calorific value of the original fuel leaves the gasifier in the form of chemical energy in carbon monoxide, methane, and hydrogen. In combustion, air containing sufficient oxygen to completely oxidize the hydrocarbon is used. The resulting gas (flue gas) is essentially all carbon dioxide, water vapor, and diluent nitrogen, and has no calorific value. The energy of the original fuel leaves the system as sensible heat that can be used for steam raising and, if required, electricity generation. Combustion offers a practical means for recovering the energy in biomass materials, using currently available technology. Further, it is well suited to small-scale utilization, a factor that seems to be of importance on account of the dispersed nature of the resource.

The properties of biomass that have a significant bearing on its thermal conversion are its relatively high moisture, oxygen, hydrogen, and volatile matter content, and low energy density. The high oxygen and hydrogen contents account for the high proportion of volatile matter and consequently high yields of gases and liquids on pyrolysis. The advantages of the high H/C ratio associated with biomass are not reflected in the products to the extent that might be expected. In fact, pyrolysis gases can be deficient in pure hydrogen and pyrolysis liquids are highly oxygenated, viscous tars.

An additional and significant source of water vapor in biomass gases is the high moisture content of the source materials. In countercurrent flow schemes such as the Lurgi moving bed gasifier, this water is evolved in the relatively low temperature drying and pyrolysis zones and does not partake in gas phase or carbon-steam gasification reactions. On the other hand, in fluidized bed systems, the moisture is evolved in the high-temperature well-mixed reaction zone and therefore does participate in the reactions. If the system is directly heated and air blown, the additional heat required to evaporate the water will result in more nitrogen being introduced, and more carbon dioxide being produced, so reducing the calorific value of the product gas. As the gas from air-blown processes is, in any case, a low-CV product, this factor is probably of little consequence other than with very wet feedstock. In oxygen-blown

systems, however, the additional pure oxygen required and higher carbon dioxide content of the medium-CV off gas may be of sufficient impact to dictate some degree of drying as a pretreatment.

Apart from drying, additional beneficiation may be undertaken to yield a resource of higher energy density. These operations will normally be undertaken at the source, so transport and subsequent storage costs may be reduced as well. Beneficiation steps include size reduction and densification. Waste heat, if available, may be used for drying, while size reduction and compression to form pellets or briquettes is estimated to require less than 2% of the energy in the dry biomass. Nevertheless, these operations are time consuming, and can be either labor or capital intensive.

Some advantages of biomass over conventional fossil fuels, not so far discussed, are their low-sulfur content and their relatively highly reactive chars. In addition, biomass materials do not cake and can therefore be easily handled in both fluidized and moving bed reactors. Finally, catalyst poisons are not present in biomass in significant concentrations. This can be important for the initial thermal processing as well as for subsequent upgrading operations.

The most suitable biomass resources for thermal conversion are wood and the organic portion of municipal solid waste. Crop residues and grasses are of intermediate value, although thermal conversion might prove more effective than fermentation. If the versatility of a liquid fuel is desired, gasification may be combined with methanol or Fischer-Tropsch synthesis.

Very wet resources such as aquatic biomass and animal wastes are not suited to thermal conversion, and are best reserved for anaerobic digestion.

See also: Combustion, Gasification, Liquefaction, Pyrolysis.

Thermal Cracking

Thermal cracking is a chemical process by which organic molecules are decomposed into lower-molecular-weight products. Thermal cracking can take place in the presence of a catalyst (catalytic cracking) or in the presence of hydrogen or a hydrogen-rich gas (hydrocracking).

The thermal cracking of carbonaceous feedstocks does not require the addition of a catalyst. This approach is the oldest technology available for feedstock conversion, and the severity of thermal processing determines the conversion and the product characteristics. As the temperature and residence time are increased, the primary products undergo further reaction to produce various secondary products, and so on, with the ultimate products (coke and methane) being formed at extreme temperatures of approximately 1,000°C (1,830°F).

Typically, carbonaceous feedstocks contain many thousands of different compounds, and this broad range in molecular weights results in boiling points that range from -160°C (-288°F) to temperatures in excess of on the order of 1,200°C (2,190°F). The higher-molecular-weight constituents of the feedstock are converted by thermal methods to lower-molecular-weight products that are refined and prepared for the market. Thus, understanding the thermal chemistry of any feedstock not only allows an explanation of the means by which products can be formed from the feedstock but also offers an option of predictability.

See: Thermal Conversion, Thermal Decomposition.

Thermal Decomposition

The thermal decomposition of carbonaceous feedstocks on a commercial scale is an old art and is often more commonly referred to as carbonization. In the process, a mix of solid, liquid, and gaseous products is usually achieved by the use of temperatures up to 1,500°C (2,730°F). The process may also be referred to as destructive distillation and has been applied to a whole range of organic materials, but more particularly to natural products such as wood, sugar, and vegetable matter to produce charcoal.

However, carbonization is a process for the production of a carbonaceous residue (coke) by the thermal decomposition (with simultaneous removal of distillate) of organic substances. The process, which is also referred to as destructive distillation, has been applied to a whole range of organic (carbon-containing) materials, particularly natural products such as wood, sugar, and vegetable matter to produce charcoal. In this present context, the

carbonaceous residue from the thermal decomposition of coal is usually referred to as coke (which is physically dissimilar from charcoal) and has the more familiar honeycomb-type structure. Thus, thermal decomposition is essentially a process for the production of volatile products as well as a carbonaceous residue by heating the feedstock (with the simultaneous removal of distillate) of organic substances.

$$[C]_{\text{organic}} = [C]_{\text{coke/char/carbon}} + \text{liquids} + \text{gases}$$

The thermal decomposition process is a complex sequence of events which can be described in terms of several important physicochemical changes, such as the tendency of the feedstock (in some cases) coal to soften and flow. In fact, some coals become quite fluid at temperatures of the order of 400 to 500°C (750 to 940°F), and there is a considerable variation in the degree of maximum plasticity, the temperature of maximum plasticity, as well as the plasticity temperature range for various coals. Indeed, significant changes also occur in the structure of the char during the various stages of devolatilization.

See also: Carbonization, Thermal Conversion.

Thermochemical Platform

The thermochemical platform typically uses a combination of pyrolysis, gasification, and catalysis to transform wood into syngas – the gaseous constituents of wood – and then into fuels or chemicals. Syngas production through pyrolysis is accompanied by the generation of char, which can then be gasified to provide process heat and energy for the thermochemical platform. A variety of commercial-scale processes exist to transform fossil fuels such as coal or natural gas into liquid fuels, including Fischer-Tropsch fuels. However, the use of biomass instead of fossil fuels changes the composition of syngas, creating a more heterogeneous intermediate product and increasing the difficulty in downstream catalysis. A range of technical problems must be overcome before biomass becomes a commercially viable substitute for fossil feedstocks in second-generation biofuel production. However, the elements of the thermochemical platform are highly suitable for bioenergy production.

This platform uses thermochemical processes to gasify wood, producing synthesis gases (sometimes called producer gases). This platform combines process elements of pretreatment, pyrolysis, gasification, clean-up, and conditioning to generate a mixture of hydrogen, carbon monoxide, carbon dioxide, and other gases. The products of this platform may be viewed as intermediate products, which can then be assembled into chemical building blocks and eventually end products.

In the thermochemical platform, the only pretreatment required involves drying, grinding, and screening the material in order to create a substrate that can easily be fed into the reaction chamber. The technology required for this stage is already available on a commercial basis, and is often associated with primary or secondary wood processing, or agricultural residue collection and distribution.

In the primary processing stage, the volatile components of biomass are subjected to pyrolysis or combustion in the absence of oxygen, at temperatures ranging from 450 to 600°C (840 to 1,110°F). Depending on how fast the pyrolysis stage is carried out, a variety of products can be achieved. If pyrolysis is carried out quickly (fast pyrolysis), a combination of vapors, condensable vapors, and char is produced. The condensation of these products creates a bio-oil which, under ideal conditions can make up 60 to 75% w/w of the original fuel mass, and can be used as feedstock for value-added chemical products, or possibly as a biofuel. If the pyrolysis is carried out at a slower rate (slow pyrolysis), the vapors that are formed are less likely to condense into bio-oil. The vapors themselves consist of carbon monoxide, hydrogen, methane, carbon dioxide, and water, as well as volatile tars.

Slow pyrolysis, like fast pyrolysis, leaves behind a solid residue of char (or charcoal), which comprises approximately 10 to 25% w/w of the original fuel mass, and processing this material requires a second gasification stage.

If the pyrolysis is carried out at the higher temperature range (550 to 600°C; 1,020 to 1,110°F), a vapor is formed which consists of carbon monoxide, hydrogen, methane, volatile tars, carbon dioxide, and water. High temperature pyrolysis leaves behind a solid residue of char (or charcoal), which makes up approximately 10 to 25% w/w of the

original fuel mass. This material can then be gasified at temperatures of 700 to 1,200°C (1,290 to 2,190°F), at which temperatures the char reacts with oxygen in order to produce carbon monoxide, or the char can be used as fuel to drive the pyrolysis process. All gaseous products from pyrolysis and gasification are generally referred to as synthesis gases (or syngas).

After the production of syngas, a number of pathways may be followed to create second-generation biofuels or other chemical, heat, or energy products. It is possible to create one potential biofuel from the thermochemical platform without a catalysis stage.

Bio-oil has been advocated as a substitute for bunker-grade heating oil, and is approved for use in district heating utility boilers in Sweden and has been mixed with coal in a co-firing facility in the United States successfully. Other biofuels may be generated by applying a catalysis stage. Methanol is one potential biofuel that can be generated through catalysis. Currently, the majority of methanol produced is being derived from natural gas. Methanol has a high octane number (129) but relatively low energy compared to gasoline (91 to 98 octane).

Conceivably, methane could be used in higher or as a stand-alone fuel, although this would require significant infrastructure changes as well as modifications to conventional engines. Because methanol has a favorable hydrogen/carbon ratio (4:1), it is often touted as a potential hydrogen source for future transportation systems.

Another potential biofuel that can be produced through the thermochemical platform is Fischer-Tropsch diesel (or biosynthetic diesel). This fuel was first discovered in 1923 and is commercially based on syngas made from coal, although the process could be applied to biomass-derived syngas.

Another potential catalytic conversion of biomass-based syngas is to higher alcohols, including ethanol. Ethanol and other higher alcohols form as by-products of both Fischer-Tropsch and methanol synthesis, and modified catalysts have been shown to provide better yields. The thermochemical platform provides the opportunity for a number of additional co-products, as well as energy in the form of heat or electricity and biofuels. Each syngas component (i.e., CO, CO₂, CH₄, H₂) may be recovered, separated, and utilized.

A variety of commercial-scale processes exist to transform fossil fuels such as coal or natural gas into liquid fuels, including Fischer-Tropsch fuels. However, the use of biomass instead of fossil fuels changes the composition of synthesis gas, creating a more heterogeneous intermediate product and increasing the difficulty in downstream catalysis. A range of technical problems must be overcome before biomass becomes a commercially viable substitute for fossil feedstocks in second-generation biofuel production, but, in general, it is felt that elements of the thermochemical platform are highly suitable for bioenergy production.

See also: Bioconversion Platform, Biofuels – Platforms, Synthesis Gas.

Thermosphere

The outermost layer of the atmosphere, the thermosphere, blocks a variety of harmful cosmic radiation including X-rays, gamma rays, and some ultraviolet radiation. Temperatures in the upper thermosphere may reach 1,500°C (2,730°F), but the number of atoms is so small at this altitude that heat energy is actually low. Isolated gas molecules in the thermosphere are broken into ions as solar radiation strips electrons from oxygen and nitrogen molecules. These ionized gases make up the ionosphere, from 50 to 250 miles. Visible effects (auroras, such as the Aurora Borealis in northern latitudes and the Aurora Australis in southern latitudes) occur when electrons and protons from the sun interact in the ionosphere.

At these high altitudes, the residual atmospheric gases sort into strata according to molecular properties, such as density. The temperature in the thermosphere increases with altitude due to absorption of highly energy solar radiation, and, in fact, the temperature is highly dependent on solar activity, and can rise to 1,700°C (3,100°F) or even higher. Radiation causes the atmosphere particles in this layer to become electrically charged particles, thereby enabling radio waves to be refracted and thus be received beyond the horizon.

The dynamics of the thermosphere are dominated by atmospheric tides, which are driven predominantly by diurnal heating. Atmospheric waves dissipate above this level because of collisions between the neutral gas and the ionospheric plasma.

See also: Atmosphere.

Thiolex/Regen Process

The Thiolex/Regen process is used to extract hydrogen sulfide, carbonyl sulfide, and mercaptans from gases and high liquid streams, including gasoline, with caustic using fiber-film contactor technology.

The caustic phase flows along the fiber-film contactor fibers, which is continuously renewed, as the wet fibers are preferentially wetted by the caustic phase in the process. Hydrocarbons flow through the shroud parallel to the caustic phase where the hydrogen sulfide and mercaptans are extracted into the caustic phase in the Thiolex section. The two phases disengage, and the caustic flows to the Regen section where the spent caustic is regenerated using air and catalyst in the oxidizer for reuse which converts the extracted mercaptans to disulfides.

The disulfides are removed from the caustic by a fiber-film contactor solvent wash system.

See also: Gas Cleaning.

Thiopaq DeSOx Process

The Thiopaq DeSOx biological process selectively removes and converts Sox in the flue gases to elemental sulfur or hydrogen sulfide. The process is a two-step biological process. It can convert sulfite and sulfate to elemental sulfur. A sodium biophosphate solution quenches and removes particulates and absorbs SOx from the flue gas. The scrubbing liquid is regenerated and recycled to the scrubber.

The heart of the Thiopaq process is the anaerobic and aerobic bioreactors. In these airlift loop reactors, the absorbed sulfite is reduced to sulfide inside the anaerobic reactor in the presence of microorganism with hydrogen. The sulfide is then oxidized under controlled conditions to elemental sulfur via the microorganisms. The produced elemental sulfur has a hydrophilic nature and is separated from the aqueous effluent in a proprietary three-phase separator.

See also: BioDeNOx Process, Gas Cleaning.

Thiopaq Hydrogen Sulfide Removal

The biological Thiopaq process selectively removes and converts hydrogen sulfide and low-boiling mercaptans from gas streams, aqueous streams, and/or low-boiling hydrocarbons to elemental sulfur or sulfate.

The Thiopaq process consists of three integrated process sections. An absorption section to remove the hydrogen sulfide from the gas stream, bioreactors, and a sulfur separation section.

The heart of this process is the bioreactor. In these air lift loop reactors, sulfide is oxidized under controlled conditions to elemental sulfur in the presence of microorganisms. These aerobic organisms use the released energy from the sulfide oxidation for metabolic processes. The elemental sulfur produced has a hydrophilic nature and is separated from the aqueous effluent in a proprietary three-phase separator. The scrubbing step to remove hydrogen sulfide from the gas streams is integrated into the Thiopaq process and regenerates the scrubbing solution, rather than its disposal. Regeneration is possible because the alkalinity consumption due to the absorption of hydrogen sulfide is compensated by the oxidation of hydrogen sulfide to elemental sulfur.

The absorber operates at the pressure of feed and a bioreactor temperature. The bioreactor operates at atmospheric pressure and 30 to 35°C. If the feed is available at a higher temperature, it requires cooling before entering the absorber.

See also: Gas Cleaning.

Thorium

Thorium is a naturally occurring, slightly radioactive element. It is widely distributed in nature with an average concentration of 10.5 ppm in the upper crust of the Earth. In general, thorium occurs in relatively small number in

thorium-enriched minerals: thorite, thorianite, monazite, bastnaesite, and thorogummite. However, the main world resources of thorium are coupled with monazite and bastnaesite.

Thorium is a radioactive element that occurs naturally in low concentrations (approximately 10 parts per million) in the Earth's crust. It is approximately three times as abundant as uranium and approximately as abundant as lead or molybdenum. Thorium in its pure form is a silvery-white heavy metal that is approximately as dense as lead. In nature, almost all thorium is thorium-232, although several additional isotopes can be present in small amounts. (Isotopes are different forms of an element that have the same number of protons in the nucleus but a different number of neutrons.) Thorium is a soft, ductile metal that is pyrophoric in powdered form. When heated in air, thorium turnings ignite and burn brilliantly with a white light.

Of the 26 known isotopes of thorium, only 12 have half-lives greater than one second, and of these only 3 have half-lives sufficiently long to warrant a concern. These key isotopes decay very slowly by emitting an alpha particle. The half-lives of thorium-232 (^{232}Th) and thorium-230 (^{230}Th), the isotopes of most concern, are long. The low specific activity of these two isotopes is an indication that these two isotopes are not highly radioactive. The health risks associated with thorium-228 (^{228}Th), which has a half-life of 1.9 years, are commonly included with those for radium-228 (^{228}Ra) because thorium-228 (^{228}Th) cannot persist for an extended period of time in the absence of radium-228 (^{228}Ra).

The nucleus of a thorium atom generally doesn't break up or fission when it is struck by a neutron, which can set off an energy-releasing chain reaction in uranium or plutonium. Instead, the neutron is absorbed; and the most common thorium nucleus, which consists of 90 protons and 142 neutrons, suddenly includes an extra unit, making it much less stable than it was before. Thorium-233 (^{233}Th) is so unstable, in fact, that even when produced in quantity, it soon decays radioactively. Within 23 minutes, half the thorium-233 (^{233}Th) atoms in any given mass will decay by emitting one negative charge each. The loss of each negative charge (a beta particle) in this fashion transforms one of the neutrons inside the affected nucleus into an additional proton. But as soon as the number of protons in a nucleus changes, the atom itself is transformed into a completely different element.

See also: Periodic Table of the Elements, Radioactivity, Radionuclides.

Tidal Barrage

A tidal barrage is a dam-like structure used to capture the energy from masses of water moving in and out of a bay or river due to tidal forces. Instead of damming water on one side like a conventional dam, a tidal barrage first allows water to flow into the bay or river during high tide, and releasing the water back during low tide. This is done by measuring the tidal flow and controlling the sluice gates at key times of the tidal cycle. Turbines are then placed at these sluices to capture the energy as the water flows in and out.

The barrage method of extracting tidal energy involves building a barrage across a bay or river that is subject to tidal flow. Turbines installed in the barrage wall generate power as water flows in and out of the estuary basin, bay, or river. These systems are similar to a hydro dam that produces Static Head or pressure head (a height of water pressure). When the water level outside of the basin or lagoon changes relative to the water level inside, the turbines are able to produce power. The basic elements of a barrage are caissons, embankments, sluices, turbines, and ship locks.

See also: Steam Turbine, Tidal Energy.

Tidal Energy

Tidal energy (also called tidal power) is a form of hydro-power that converts the energy of tides into electricity or other useful forms of power. The tidal forces are periodic variations in gravitational attraction exerted by celestial bodies. These forces create corresponding motions or currents in the oceans of the Earth. Due to the strong attraction to the oceans, a bulge in the water level is created, causing a temporary increase in sea level. When the sea level is raised, water from the middle of the ocean is forced to move toward the shorelines, creating a tide. This occurrence takes place in an unflinching manner, due to the consistent pattern of the moon's orbit around the Earth.

In terms of alternative energy, tidal energy refers to the energy that is harnessed from the tides for practical purposes. The term tidal power is used synonymously as the conversion of tidal energy into a useful form of energy, or more specifically as the generation of electricity from the tides. Tidal power is the only technology that draws on energy inherent in the orbital characteristics of the Earth-Moon system, and to a lesser extent in the Earth-Sun system. Tidal power may be considered a form of hydropower whereby the definition of hydropower is expanded to encompass any type of energy gained from the movement of water. Furthermore, because the Earth's tides are ultimately due to gravitational interaction with the Moon and Sun and the rotation of the Earth, tidal power is practically inexhaustible and classified as a renewable energy resource.

Although not yet widely used, tidal power has potential for future electricity generation. Tides are more predictable than wind energy and solar power. Among sources of renewable energy, tidal power has traditionally suffered from relatively high cost and limited availability of sites with sufficiently high tidal ranges or flow velocities, thus constricting its total availability. However, many recent technological developments and improvements, both in design (e.g., dynamic tidal power, tidal lagoons) and turbine technology (e.g., new axial turbines, cross flow turbines), indicate that the total availability of tidal power may be much higher than previously assumed, and that economic and environmental costs may be brought down to competitive levels.

Because the tidal strength varies greatly depending on location as well as the time of year. Tidal power traditionally involves erecting a dam across the opening to a tidal basin. The dam includes a sluice that is opened to allow the tide to flow into the basin; the sluice is then closed, and as the sea level drops, traditional hydro-power technologies can be used to generate electricity from the elevated water in the basin. In this report, there are three ways of using tidal power, which is tidal stream generator, tidal barrage, and dynamic tidal power.

There are different means to harness tidal energy – the first is to exploit the cyclic rise and fall of the sea level using barrages and the second is to harness local tidal currents, analogous to wind power also called marine current turbine. The generation of tidal energy has same method as it is in the hydroelectric power plants. There are currently three different ways to get tidal energy which are: (i) tidal streams, (ii) barrages, and (iii) tidal lagoons.

Tidal currents below the surface of the water can be harnessed using turbines; however, this often doesn't produce very much energy due to the small area of effect. The advantage of this method is that the machines needed are low cost, have minimal impact on the environment, and do not require further infrastructure.

Another way to harvest tidal energy is with a tidal barrage (also known as impoundment tidal energy), which uses a dam built beneath the water that utilizes tides to gather water. This then water flows through the dam and powers turbines. These dams have a moderate environmental impact, however, leading to the alternative tidal lagoon.

These lagoons are built near bodies of water that will be brought in by the tide to fill them. The water can then flow back into the body of water and power turbines on its way out. Because they don't need to be directly in bodies of water, tidal lagoons are more environmentally friendly. Finally, dynamic tidal power is a way to make normally unusable tides practical. It involves building a bent T-shaped dam out from a coast, and then allowing a head to form on either side of the dam due to tidal shifts from the moon. These would power bi-directional turbines as they leveled out, resulting in a reliable source of energy. This is, however, one of the most expensive forms of tidal energy leading it to be less practical.

For most tidal energy generators, turbines are placed in tidal streams. A tidal stream is a fast-flowing body of water created by tides. A turbine is a machine that takes energy from a flow of fluid. That fluid can be air (wind) or liquid (water). Because water is much more dense than air, tidal energy is more powerful than wind energy. Unlike wind, tides are predictable and stable. Where tidal generators are used, they produce a steady, reliable stream of electricity.

Placing turbines in tidal streams is complex, because the machines are large and disrupt the tide they are trying to harness. The environmental impact could be severe, depending on the size of the turbine and the site of the tidal stream. Turbines are most effective in shallow water. This produces more energy and allows ships to navigate around the turbines. The turbine blades of a tidal generator also turn slowly, which helps marine life avoid getting caught in the system.

Another type of tidal energy generator uses a large dam called a barrage. With a barrage, water can spill over the top or through turbines in the dam because the dam is low. Barrages can be constructed across tidal rivers, bays, and estuaries. Turbines inside the barrage harness the power of tides the same way a river dam harnesses the power of a river. The barrage gates are open as the tide rises. At high tide, the barrage gates close, creating a pool, or tidal lagoon. The water is then released through the turbines of the barrage, thereby creating energy at a rate that can be

controlled. The doors and the turbines installed along a barrage or dam extend through the opening of the tidal basin, such as an estuary or a dam. A diverse level of fluid is produced on the sides of the barrage by the tides. The doors are opened as this difference gets increased, causing the water to flow out. This water thus strikes with turbine blades and causes them to rotate, and electric power is generated.

The environmental impact of a barrage system can be quite significant. The land in the tidal range is completely disrupted. The change in water level in the tidal lagoon might harm plant and animal life. The salinity inside the tidal lagoon lowers, which changes the organisms that are able to live there. As with dams across rivers, fish are blocked into or out of the tidal lagoon. Turbines move quickly in barrages, and marine animals can be caught in the blades. With their food source limited, birds might find different places to migrate. A barrage is a much more expensive tidal energy generator than a single turbine. Although there are no fuel costs, barrages involve more construction and more machines. Unlike single turbines, barrages also require constant supervision to adjust power output.

The final type of tidal energy generator involves the construction of tidal lagoons. A tidal lagoon is a body of ocean water that is partly enclosed by a natural or manmade barrier. Tidal lagoons might also be estuaries and have fresh-water emptying into them. A tidal energy generator using tidal lagoons would function much like a barrage. Unlike barrages, however, tidal lagoons can be constructed along the natural coastline. A tidal lagoon power plant could also generate continuous power. The turbines work as the lagoon is filling and emptying.

The technology that is used to produce electricity using the difference between the low and high tides is similar to the one use on the generation of electricity on the traditional hydroelectric power plants. The use of the tidal energy requires a dam or barrage across a shallow area, preferably an estuary, bay or gulf of high tidal range where the difference on the low and high tide have to be at least 5 meters. The tide basins are filled and empty every day with the flood tides when the water level rises and with the ebb tides when the water level falls. On the barrage, there are low-head turbines and sluices gates that allow the water to flow from one side of the barrage to inside the tidal basin. This difference on elevation of the water level creates a hydrostatic head that generates electricity. There are different modes to generate electricity using the barrage systems: (i) ebb generation, (ii) flood generation, (iii) two-way generation, (iv) pumping, and (v) double basin.

Using the ebb generation method, the incoming water (flood tide) is allowed to flow freely to fill the basin until high tide, then the sluices are close and water are retained on one side of the barrage. When the level of the water outside of the barrage decreases (ebb tide) sufficiently to create a hydrostatic head between the open waters and the tide basin, the sluices are open and water flows through the turbines and generate electricity. Once the head is low, the sluices gates are open and the basin is filled again.

Using the flood generation method, during the flood tide, the sluices gates and low-head turbines are kept closed to allow the water level outside of the barrage to increase. Once a hydrostatic head is created, the sluices gates are opened and the water flows through the turbines into the basin. This mode is less efficient than the ebb mode.

The two-way generation method uses both the ebb and the flood tide to generate electricity. The main problem with this type of mode is that the turbines must work both ways when water enters or exits the basin. On the pumping generation method, the hydrostatic head can be increased, reversing the power and turning the turbine-generator into a pump-motor. During the generation, the energy that was use is returned.

In the flood generation method, the basin is filled through the turbines, which generate at tide flood. This is generally much less efficient than ebb generation because the volume contained in the upper half of the basin (which is where ebb generation operates) is greater than the volume of the lower half (filled first during flood generation). Therefore the available level difference in turbine power produce – between the basin side and the sea side of the barrage – reduces more quickly than it would in ebb generation. Rivers flowing into the basin may further reduce the energy potential, instead of enhancing it as in ebb generation.

In the pumping method, turbines are able to be powered in reverse by excess energy in the grid to increase the water level in the basin at high tide (for ebb generation). This energy is more than returned during generation because power output is strongly related to the head. If water is raised 2 ft. (61 cm) by pumping on a high tide of 10 ft. (3 m), this will have been raised by 12 ft. (3.7 m) at low tide. The cost of a 2 ft. rise is returned by the benefits of a 12 ft. rise. This is since the correlation between the potential energy is not a linear relationship, rather, is related by the square of the tidal height variation.

Another form of energy barrage configuration is that of the dual basin type. With two basins, one is filled at high tide and the other is emptied at low tide. Turbines are placed between the basins. Two-basin schemes offer

advantages over normal schemes in that the generation time can be adjusted with high flexibility, and it is also possible to generate almost continuously. In normal estuarine situations, however, two basin schemes are expensive to construct due to the cost of the extra length of barrage. There are some favorable geographies, however, which are well suited to this type of scheme.

Tidal pools are independent enclosing barrages built on high-level tidal estuary land that trap the high water and release it to generate power. Two lagoons operating at different time intervals can guarantee continuous power output. Enhanced pumped storage tidal series of lagoons raises the water level higher than the high tide, and uses intermittent renewable energy for pumping.

While the methods described above use one tidal basin, in the double basin method, the turbines are placed between the basins. The main basin will use the ebb generation mode to operate and pump water with part of the energy that is generated to and from the second basin to generate electricity continuously.

The environmental impact of tidal lagoons is minimal. The lagoons can be constructed with natural materials like rock. They would appear as a low breakwater (sea wall) at low tide, and be submerged at high tide. Animals could swim around the structure, and smaller organisms could swim inside it. Large predators like sharks would not be able to penetrate the lagoon, so smaller fish would probably thrive. Birds would likely flock to the area. However, the energy output from generators using tidal lagoons is likely to be low.

See also: Ocean Energy, Steam Turbine, Wave Energy.

Tidal Stream Generator

A tidal stream generator, often referred to as a tidal energy converter (TEC), is a machine that extracts energy from moving masses of water, in particular tides, although the term is often used in reference to machines designed to extract energy from run of river or tidal estuarine sites.

Tidal stream generators draw energy from water currents in much the same way as wind turbines draw energy from air currents. However, the potential for power generation by an individual tidal turbine can be greater than that of similarly rated wind energy turbine. The higher density of water relative to air (if the density of air = 1, the density of water = approximately 800) means that a single generator can provide significant power at low tidal flow velocities compared with similar wind speed. Also, since power varies with the density of medium and the cube of velocity, water speeds of nearly one-tenth the speed of wind provide the same power for the same size of turbine system; however, this limits the application in practice to places where tide speed is at least 2 knots (1 meter per second) even close to a neap tide, which is a tide that occurs just after the first or third quarters of the moon when there is least difference between high and low water. Furthermore, at higher speeds in a flow between 2 and 3 meters per second in seawater, a tidal turbine can typically access four times as much energy per rotor swept area as a similarly rated power wind turbine.

Tidal stream generators are the least ecologically damaging among the three main forms of tidal power generation. Various turbine designs have varying efficiency and therefore varying power output.

See also: Tidal Energy

Timber Belts

Wood is an organic material, a natural composite of cellulose fibers embedded in a matrix of lignin. Wood is produced as secondary xylem in the stems of trees. Wood is one of the most abundant and environmentally friendly biomass resources.

The main advantage of using wood as a fuel is that wood is a renewable resource, offering a sustainable, dependable supply. Other advantages include the fact that the amount of carbon dioxide (CO₂) emitted during the burning process is typically 90% less than when burning fossil fuel. Wood fuel contains minimal amounts of sulfur and heavy metals, and use of wood as a fuel is not a threat to pollution by acid rain, and particulate emissions are controllable.

Timber belts are multiple row field windbreaks that are planted with commercially valuable, fast-growing trees (such as hybrid poplar or hybrid willow) to provide conservation benefits, improve adjacent crop yields, diversify

on-farm income sources, and produce commercially valuable wood products. Various planting configurations have been developed that provide wind protection for soils and crops, and yield sufficient biomass to make wood harvest economical. Tree rows are oriented perpendicular to the prevailing wind to reduce wind velocity and improve the microclimate within the sheltered zone to enhance the production of adjacent crops. Because of their rapid growth and range of marketable products, hybrid poplars fit well into the timber belt concept. The strategy is to harvest half of the rows in a timber belt at age 7 to 12, while the other half are left to provide continued wind protection. Within a few years after the stumps have sprouted and re-established sufficient wind protection, the remaining rows are harvested. In this way, continuous wind protection and associated economic benefits to adjacent crops can be achieved.

See also: Biomass, Timberland, Wood, Wood Biomass.

Timberland

Forest land is land that is 10% forested by trees of any size and includes land that may have been naturally or artificially regenerated. Thus, timberland is forest land that is available to harvest and capable of productivity over a long period of time in terms of producing or is capable of producing crops of industrial wood, and that is not withdrawn from timber utilization by statute or administrative regulation.

See also: Biomass, Timber Belts, Timberland, Wood, Wood Biomass.

Tires – Devulcanization

Goodyear Rubber and Tire Company developed a unique process for devulcanizing scrap tire rubber using a novel supercritical fluid technology.

The technology uses sec-butanol [2-butanol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$] as a supercritical fluid, which functions as a pyrolysis medium and also as a chain cleavage agent. The solvent not only facilitates the cleavage of carbon-sulfur (C-S) and carbon-carbon (C-C) bonds reaction in a near-homogeneous state, but also dissolves the reacted fragments and takes them away from other reactive intermediates. The solvent, sec-butanol, is fully recoverable and reusable in the process.

This strong supercritical behavior of sec-butanol may be attributed to its unique molecular structure which has the center carbon connected to all four different functional fragments, thereby maximizing the quadruple moments. They further enhanced their process by employing a co-solvent process, by which the amount of sec-butanol needed can be significantly reduced for the process without losing the efficiency. As a co-solvent to this process, carbon dioxide was found to be effective.

See also: IFP Process, Tires – Dry Distillation, Tires – Scrap.

Tires - Dry Distillation

The dry distillation of spent tires can be operated with either shredded or whole tires without removing metallic wires.

The tires enter the top of the distillation tower via a conveyor belt. Once filled, the tower is sealed to prevent the gaseous product from escaping. Combustion is initiated by burners located at the bottom of the tower and then sustained by the introduction of process air. As combustion continues, the hot gas rises to the top of the tower. The rising gas has a dual purpose. The first is to assist in the combustion of the tires located at the top of the tower. Secondly, the rising of the gas acts in the same manner as a traditional distillation column for the separation of the end products. The gas is cooled down by the gas cooler. Part of the gas is liquefied and recovered in the form of oil. Recovered oil is equivalent to Class B heavy oil. The residue (char and tire cord) is removed from the bottom tower by a conveyor. Once cooled, the residue is separated into individual components.

See also: IFP Process, Tires – Scrap.

Tires – Hydrogenation

Hydrogenation, unlike pyrolysis or similar processes, is a chemical synthesis process. In simplistic terms, it entails the addition of hydrogen, the element, which is removed from oil, to make synthetic rubber. By adding the appropriate amount of hydrogen to the waste tires, the rubber can be returned to its original form.

By adding hydrogen, devulcanization, saturation, carbon-carbon bond cleavage reactions are induced. In some sense, the process is quite similar to the hydrotreating process of heavy oil and residua.

See also: Hydroprocesses.

Tires – Pyrolysis

In the process, the scrap tires are first reduced in size, by grinding, chipping, or pelletizing, then sent to a clarifier for the removal of the scrap metal.

The method involves use of a temperature is initially at 100°C, while the rubber is loaded into the reactor. After one hour, the temperature is ramped to 300-500 °C, depending on the process. The reactor is held at the final temperature for a minimum of two hours. The gas fraction is sent to a distillation apparatus for subsequent purification and analysis. The oil and char are separated using a second column.

See also: Tires – Scrap.

Tires – Scrap

The United States alone generates over millions of waste tires each year. Although numerous recycling programs and methods have been deployed over the years, a large percentage of these tires still end up in landfills. Scrap tires are almost immune to biodegradation and will survive in landfills for years, if not decades.

Converting these waste tires into usable energy through environmentally responsible technology provides a significant opportunity (Table T-1).

Table T-1 Scrap tire pyrolysis.

Feedstock	Process	Products	Process	Use
Scrap tires	Pyrolysis	Gases	Gas cleaning	Heat and power
Oil	Refining	Fuel oil		
		Char	Purification	Activated carbon
				Filler

Waste tire pyrolysis involves the thermal degradation in the absence of oxygen. The benefit of this application is the conversion of waste tires into value-added products such as olefins, chemicals, and surface-activated carbon.

The production of significant quantities of valuable high-molecular-weight olefins to obtain curable and moldable olefins (molecular weight >15,000) would overcome current economic barriers. These are typically produced in small quantities because the process temperature is high. At high temperature, vulcanized rubbers are quickly decomposed to low-molecular-weight olefins (Mw 300-400). High-molecular-weight compounds can be generated by low-temperature pyrolysis. However, lower temperature will require longer process times. New technological breakthroughs will be necessary for the commercialization of low-temperature pyrolysis. Other technologies that are being developed include (i) microwave pyrolysis, (ii) ultrasonic devulcanization, (iii) supercritical fluid depolymerization, and (iv) catalytic processes.

Microwave pyrolysis is the use of microwaves to heat objects more uniformly than conventional heating methods. Microwave heating requires shorter heating times. Microwave pyrolysis will result in relatively high-molecular-weight olefins and a high proportion of valuable products such as ethylene, propylene, butene, aromatics, etc. The

short process time also contributes to a reduction in the process cost. Moreover, for microwave heating, the shape of the tire chip is less important compared to the requirements of conventional heating. Whole tires or larger chips can be processed using microwave pyrolysis, which greatly reduces pre-processing cost.

Ultrasonic devulcanization involves the use of sonic energy to break down sulfur-carbon chemical bonds in tires. Chipped tires are heated to approximately 200°C (390°F) then subjected to 20,000 cycles per second of ultrasonic energy (just above the highest frequency the human ear can discern) at pressures reputedly up to several thousand pounds per square inch. The rubber is transformed from a solid to a highly viscous fluid within milliseconds. With additional curative agents, the viscous material can be molded into new products.

Supercritical water can be used to controllably depolymerize the rubber compounds. This approach requires lower temperatures (approximately 400°C, 750°F) and shorter processing times. Tire compounds are decomposed to high-molecular-weight olefins or oil.

Use of catalysts can reduce processing temperature or time. Reduced temperature and time can result in either higher-molecular-weight olefins or an increasing proportion of valuable substances. The advantage of catalysts is that no new equipment or knowledge is required.

See also: Waste, Municipal Solid Waste, Pyrolysis.

Ton, Tonne

One U.S. ton (short ton) is equivalent to 2,000 pounds. One Imperial ton (long ton or shipping ton) is equivalent to 2,240 pounds.

One metric ton (tonne) is equivalent to 1,000 kilograms (2,205 pounds). One oven-dry ton or tonne (ODT, sometimes termed bone-dry ton/tonne) is the amount of wood that weighs one ton/tonne at 0% moisture content.

One green ton/tonne refers to the weight of undried (fresh) biomass material – the moisture content must be specified if green weight is used as a fuel measure.

Torrefaction

Untreated woody biomass has a relatively low energy density, high moisture content and is difficult to comminute into small particles. These properties make the transport of wood relatively expensive. After drying, it can regain moisture and may rot during storage. Furthermore, enhancement of the energy density is advisable because a large amount of wood is required to replace an equivalent amount of coal in applications such as combustion and gasification. A technology that could help to overcome these problems is a thermal processing step known as torrefaction.

Torrefaction represents the thermal treatment of biomass (mainly wood) in the absence of oxygen for 15-60 min at 200 to 300°C (390 to 570°F) and at atmospheric pressure. As a result, biomass (such as wood) is converted into a carbonaceous product. Torrefaction transformation is highly efficient – with an 85 to 95% conversion rate.

The energy spent on torrefaction is fully paid off by the 8 to 10 times lower energy consumption of torrefied wood milling compared to fresh wood milling. As the properties of torrefied wood and coal are similar, the conventional coal-feeding facilities can be used for torrefied wood.

In terms of the process, torrefaction is a mild thermal treatment at a temperature of 250 to 300°C (480 to 570°F), which converts solid biomass into a more brittle and easily pulverized material that can be treated and handled just like coal. This torrefied product is often called bio-coal.

Pulverized torrefied biomass can be treated just as coal, and most entrained flow gasifiers designed for coal can be smoothly converted for torrefied bio-coal without much adaptation. The gases produced during the torrefaction process may be used for torrefaction, thus accomplishing a self-energy supply cycle.

Dehydration and decarboxylation reactions cause a mass loss of the wood, whereas the lower heating value of the wood is largely conserved. Deciduous wood types (beech and willow) and straw were found to produce more volatiles than coniferous wood (larch), especially more methanol and acetic acid. These originate from acetoxy-groups and from methoxy-groups present as side chains in xylose units present in the xylan-containing hemicellulose fraction.

The torrefied wood product has a brown/black color, reduced volatile content, and increased energy density. It has favorable properties for application as a fuel for gasification and/or (co-)combustion.

The chemical properties of torrefied wood could also be related to its mechanical properties, depending on the extent of decomposition of the hemicellulose fraction in the torrefaction process (and possibly depolymerization of the cellulose fraction); the friability can be expected to increase.

See also: Biomass, Wood, Wood – Thermal Treatment.

Town Gas

The term town gas is a generic term referring to manufactured gas produced for sale to consumers and municipalities. The terms coal gas, manufactured gas, producer gas, and syngas (synthetic natural gas, SNG) are also used for gas produced from coal. Depending on the processes used for its creation, town gas is a mixture of hydrogen, carbon monoxide, methane, and volatile hydrocarbons with small amounts of carbon dioxide and nitrogen as impurities. Town gas has a heat content of approximately 600 Btu/ft³.

Prior to the development of natural gas supplies and transmission in the United States during 1940s and 1950s, virtually all fuel and lighting gas was manufactured, and the by-product coal tar was an important feedstock for the chemical industry. The development of manufactured gas paralleled that of the industrial revolution and urbanization.

Toxicity Characteristic Leaching Procedure

The toxicity characteristic leaching procedure (TCLP) is a soil sample extraction method for chemical analysis.

Landfill leachate is a notoriously complex substance to deal with, primarily because of its ever-changing composition. In that sense, the TCLP is a procedure for determining the decay of release of a material from a landfill and can be used as a gauge of the decay of organic material to produce liquids and landfill gas.

The toxicity characteristic leaching procedure comprises four fundamental procedures which are (i) sample preparation for leaching, (ii) sample leaching, (iii) preparation of leachate for analysis, and (iv) leachate analysis and is generally useful for classifying waste material for disposal options. Extremely contaminated material is expensive to dispose, and grading is required to ensure safe disposal and to avoid paying for disposal of clean fill. The main problem is that the toxicity characteristic leaching procedure test is based on the assumption that the waste material will be buried in landfill along with organic material. Organic matter is not really buried with other waste anymore (composting usually applies), and other leachate techniques may be more appropriate.

As an example of the method, the pH of the sample material is first established, and then leached with an acetic acid/sodium hydroxide solution at a 1:20 mix of sample to solvent. The leachate solution is sealed in extraction vessel for general analytes, or possibly pressure sealed as in zero-headspace extractions (ZHE) for volatile organic compounds, cyanides, or sulfites, and tumbled for 18 hours to simulate an extended leaching time in the ground.

To date, landfill leachate has not been designated as a potential biofuel source (because of the complex variables that dictate the composition of the leachate) but that time may arise after stricter regulations regarding waste segregation are enacted.

See also: Landfill Gas, Landfilling, Landfill Leachate.

Trace Element

A trace element is a chemical element whose concentration is less than 1,000 ppm w/w or 0.1% w/w of the composition of the substance. Many types of biomass contain trace of elements. Trace elements also known as trace minerals, are the chemical components that naturally occur in soil, plant, and wildlife in minute concentrations. They are necessary for the optimal development and metabolic functioning such as proper cell metabolism, effective immune function, and healthy reproduction of humans. Their role and homeostasis in living organisms vary. There are 19

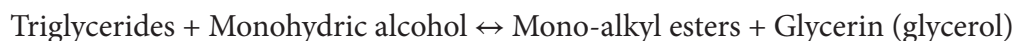
known trace elements that are categorized into three groups: (i) essential elements, (ii) probably essential elements, and (iii) potentially toxic elements.

Many trace elements are concentrated in particulate emissions; it is these extremely small particles that are the most difficult to eliminate and which are potentially the most harmful since they have the ability to enter, directly or indirectly, the human physiological system.

Transesterification

Transesterification is a chemical process in which an alcohol reacts with the triglycerides in vegetable oil or animal fats, separating the glycerin and producing biodiesel.

The purpose of transesterification of vegetable oils to their methyl esters (biodiesel) process is to lower the viscosity of the oil. The transesterification reaction is affected by alcohol type, the molar ratio of glycerides to alcohol, the type and amount of catalyst, reaction temperature, reaction time, and free fatty acids and the water content of vegetable oils or animal fats. The transesterification reaction proceeds with or without a catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms as follows:



Generally, the reaction temperature near the boiling point of the alcohol is recommended. The reactions take place at low temperatures [approximately 65°C, 150°F] and at modest pressures (30 psi). Biodiesel is further purified by washing and evaporation to remove any remaining methanol. The oil (87%), alcohol (9%), and catalyst (1%) are the inputs in the production of biodiesel (86%), the main output. Pretreatment is not required if the reaction is carried out under high pressure and high temperature (240°C, 465°F), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60 to 80°C (140 to 175°F) at a molar ratio of 6:1.

Vegetable oil-based biodiesel has been shown to be comparable to conventional diesel. It has low viscosity, low flash points, high vapor pressure, and is easy to process. Animal fats are preferred to vegetable oils because they are much cheaper and there is a much larger supply. Animal fats cannot be used directly because their physical properties cause poor atomization, poor vapor-air mixing, low pressure, incomplete combustion, and engine deposits. Transesterification is a means to improve all of these disadvantages. Biodiesel from animal fats have higher calorific values and cetane numbers but are less stable to oxidation and have a higher cold filter plugging point as compared to biodiesel from vegetable oils.

In the conventional synthesis of biodiesel, bio-esters (bio-oils) undergo transesterification in the presence of methanol and base (usually sodium hydroxide) (Figure 10.2). In this reaction, the bio-oil (a tri-ester or triglyceride) reacts with methanol and a catalyst to produce glycerol and three new methyl-substituted esters. Mechanistically, the triglyceride derivatives are converted to diglyceride derivatives, which are in turn converted to monoglycerides. Finally, the monoglyceride is converted to glycerol. A high ratio of methanol to oil is required for transesterification. The high ratio of methanol also helps the glycerol that is formed phase separate (Figure 10.3). Once the glycerol phase separates from the biodiesel, the biodiesel is purified via water washing, vacuum drying, and filtration. The energy-intensive purification of the biodiesel is one of the many reasons its processing is not energy efficient. The alcohols employed in the transesterification are generally short chain alcohols such as methanol, ethanol, propanol, and butanol. It was reported that when transesterification of soybean oil using methanol, ethanol, and butanol was performed, 96–98% of ester could be obtained after 1 hour.

Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol to produce methyl esters as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as iso-propanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction.

Any free fatty acids in the base oil are either (i) the fatty acids are converted to soap and removed from the process, or (ii) the fatty acids are esterified (yielding more biodiesel) using an acidic catalyst. After this processing, unlike

straight vegetable oil, biodiesel has combustion properties similar to those of diesel produced from crude oil, and can replace it in most current uses.

A by-product of the transesterification process is the production of glycerin (glycerol). For every unit of biodiesel that is manufactured, 0.1 unit of glycerol is produced. Originally, there was a valuable market for the glycerol, which assisted the economics of the process as a whole. However, with the increase in global biodiesel production, the market price for this crude glycerol (containing 20% water and catalyst residues) is lower and affords an operational challenge. Usually, the crude glycerol has to be purified, typically by performing vacuum distillation after which the refined glycerol (>98% purity) can then be utilized directly, or converted into other products.

Production of biodiesel is dependent upon a number of variables. These include: (i) the types of feedstock, (ii) catalyst, (iii) solvent, (iv) temperature and pressure, and (v) ratio of alcohol to oil. The feedstock usually includes animal tallow (animal fat) and waste cooking vegetable oil. Most studies on animal tallow focus on freshly collected animal tallow, which is low in free fatty acid value. If the animal tallow is not immediately converted, the acid value increases due to hydrolysis caused by the presence of water and degradation. Free fatty acids can react with basic catalysts, thus using up the catalyst, and the so-called soap products are difficult to separate from the desired biodiesel. Waste cooking oils also have higher amounts of free fatty acids and higher levels of moisture.

The high levels of moisture and free fatty acids are usually dealt with through some sort of acidic pre-treatment that causes acid catalysed transesterification of the free fatty acids, followed by alkaline transesterification of the bio-oils. Numerous studies, in fact, have introduced an acidic pre-treatment or simply used an acidic catalyst when the feedstock has a large amount of free fatty acids. For example, a recent study has indicated that an acidic pre-treatment (2% w/w H_2SO_4 , 65°C/149°F, 5 hours, 6:1 methanol to lard) of highly acidic animal tallow, followed by conventional biodiesel production, led to a biodiesel product with 66.2% w/w yield of approximately 96% purity.

Alcoholysis

The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol, and butanol (alcoholysis) has proved to be the most promising process.

The transesterification process is used to produce biodiesel from biomass, or some alternative source as opposed to crude oil-derived biodiesel. Biodiesel is advantageous compared to conventional biodiesel in that it is renewable, biodegradable, non-toxic, and has low emissions. Recent research has suggested that biodiesel can be produced from waste oils such as used cooking vegetable oil and from inedible animal tallow collected from slaughterhouses and other meat processing units.

Vegetable oil-based biodiesel has been shown to be comparable to conventional diesel. It has low viscosity, low flash points, high vapor pressure, and is easy to process. Animal fats are preferred to vegetable oils because they are much cheaper and there is a much larger supply. Animal fats cannot be used directly because their physical properties cause poor atomization, poor vapor-air mixing, low pressure, incomplete combustion, and engine deposits. Transesterification is a means to improve all of these disadvantages. Biodiesel from animal fats have higher calorific values and cetane numbers but are less stable to oxidation and has a higher cold filter plugging point as compared to biodiesel from vegetable oils.

In the conventional synthesis of biodiesel, the transesterification occurs in the presence of methanol and base (usually sodium hydroxide). In this reaction, the bio-oil (a tri-ester or triglyceride) reacts with methanol and a catalyst to produce glycerol and three new methyl-substituted esters. Mechanistically, the triglycerides are converted to diglycerides, which are in turn converted to monoglycerides. Finally, the monoglyceride is converted to glycerol. A high ratio of methanol to oil is required for transesterification. The high ratio of methanol also helps the glycerol that is formed phase separate. Once the glycerol phase separates from the biodiesel, the biodiesel is purified via water washing, vacuum drying, and filtration. The energy intensive purification of the biodiesel is one of the many reasons its processing is not energy efficient.

Production of biodiesel is dependent upon a number of variables. These include (i) the feedstock, (ii) the catalyst, (iii) the solvent, (iv) the temperature and the pressure, and (v) the ratio of alcohol to the oil.

The feedstock usually includes animal tallow (animal fat) and waste cooking vegetable oil. Most studies on animal tallow focus on freshly collected animal tallow, which is low in free fatty acid value. If the animal tallow is not immediately converted, the acid value increases due to hydrolysis caused by the presence of water and degradation. Free fatty acids can react with basic catalysts, thus using up the catalyst, and the so-called soap products are difficult

to separate from the desired biodiesel. Waste cooking oils also have higher amounts of free fatty acids and higher levels of moisture.

The high levels of moisture and free fatty acids are usually dealt with through acidic pre-treatment that causes acid-catalyzed transesterification of the free fatty acids, followed by alkaline transesterification of the bio-oils. Numerous studies, in fact, have introduced an acidic pre-treatment or simply used an acidic catalyst when the feedstock has a large amount of free fatty acids.

Conventionally, alkaline bases are used as the *catalyst* for transesterification; however, acidic catalysts are also beginning to be used. Common basic catalysts used include sodium hydroxide, potassium hydroxide, or their alkoxides or carbonates. Acidic catalysts commonly used are sulfuric acid and hydrochloric acid. Novel enzymatic catalysts are being tested, and scientific literature indicates that they show excellent activity and reduction in undesired co-products; however, they have significantly higher production costs.

Typically, homogenous strong bases are used as the catalyst for biodiesel production; however, there have been numerous studies on heterogeneous catalysts. Heterogeneous catalysts are preferred in large-scale productions because of their ease of separation. Obviously, any new catalyst must be inexpensive since the final product (biodiesel) must be inexpensive. Thus, egg shells have been proposed as potential catalysts for biodiesel production. When 3% w/w calcined egg shells (1,000°C, 1,830°F, 2 hours) were added to a 9:1 molar ratio mixture of methanol and oil, the biodiesel yield exceeded 95% after three hours. The reaction conditions and yield are similar to the homogenous catalytic reaction, and there is, in this case, the benefit of using a low-cost, heterogeneous catalyst.

The most common alcohols used are methanol and ethanol; however, methanol is used more frequently because it is lower in cost. When methanol is used as the solvent, the products are methyl esters. Ethanol is being further investigated because the viscosities of ethanol-ethyl ester mixtures are lower, and ethanol can be produced from renewable or waste resources. Furthermore, ethanol separates from glycerol more effectively.

Transesterification can occur at room temperature if the reaction is left long enough. However, usually, the temperature is kept close to the boiling point of the alcohol used at atmospheric pressure. It has been noted, though, that optimal reaction temperature and pressures depend upon the type and quality of the waste cooking oil being processed. Alcohol in excess of the stoichiometric proportion necessary is commonly used. For acid-catalyzed conversion of oils with high amounts of free fatty acids, much higher ratios are used compared to base-catalyzed transesterification. Specifically, the ratios can range from 6:1 alcohol to oil for base-catalyzed esterification all the way to 250:1 for acid-catalyzed reactions.

Biodiesel produced from waste has been shown to be comparable to biodiesel produced from conventional sources. For example, the engine performance by tallow biodiesel is comparable with the performance by pure diesel fuel without any engine modifications in a direct injection diesel engine. However, tallow biodiesel cannot be used in cold weather conditions because of its low pour point. If the fuel product is used in boilers for heat generation, it can be used without mixing with conventional biodiesel. Furthermore, biodiesel can be mixed until desired qualities are achieved. For example, blending 20% v/v animal-fat derived biodiesel with conventional diesel produces a cetane number higher than conventional diesel.

Using wastes as sources for biodiesel has several major advantages: (i) avoid the fuel versus food debate since the feedstock is non-edible, (ii) reduce the final cost of the fuel since non-edible feed stock is typically cheaper, (iii) recycle waste, and (iv) the produced fuel is biodegradable. However, the production of biodiesel also has its disadvantages. Transesterification is normally achieved using alkaline catalysts. These catalysts are corrosive and form unwanted by-products that are expensive to separate. Homogenous acid catalysts can also be used, but these are difficult to recycle, operate at high temperatures, and have significant corrosion and environmental issues.

Recently, a catalyst-free method was developed for biodiesel production by employing supercritical methanol. The supercritical treatment at 350°C (650°F) and approximately 6,000 psi with a molar ratio of 42 in methanol is the optimum condition for transesterification of rapeseed oil to biodiesel fuel.

To achieve more moderate reaction conditions, further effort was made through the two-step preparation. In this method, oils/fats are, first, treated in subcritical water for hydrolysis reaction to produce fatty acids. After hydrolysis, the reaction mixture is separated into oil phase and water phase by decantation. The oil phase (upper portion) is mainly fatty acids, while the water phase (lower portion) contains glycerol in water. The separated oil phase is then mixed with methanol and treated at supercritical condition to produce FAME thorough methyl esterification. After removing unreacted methanol and water produced in reaction, FAME can be obtained as biodiesel. Therefore, in

this process, methyl esterification is the main reaction for FAME formation, while in the one-step method, transesterification is the major one.

Reaction by supercritical methanol has some advantages such as (i) glycerides and free fatty acids are reacted with equivalent rates, (ii) the homogeneous phase eliminates diffusive problems, (iii) the process tolerates great percentages of water in the feedstock catalytic process require the periodical removal of water in the feedstock or in intermediate stage to prevent catalyst deactivation, (iv) the catalyst removal step is eliminated, and (v) if high methanol/oil ratios are used, total conversion of the oil can be achieved in a few minutes. Some disadvantages of the one-stage supercritical method are clear and are (i) the process operates at very high pressures, (ii) the high temperatures used in the process bring along proportionally high heating and cooling costs, (iii) high methanol/oil ratios, which are typically set at 42 and involve high costs for the evaporation of the unreacted methanol, and (iv) the process as posed to date does not explain how to reduce free glycerol to less than 0.02% as established in a variety of international standards.

Biodiesel can be used in any application where conventional diesel is used. For example, tests in light and heavy trucks showed few differences other than the requirement for more frequent oil changes because of build-up in an engine crankcase. Using wastes as sources for biodiesel has several major advantages: (i) avoid the fuel versus food debate since the feedstock is non-edible, (ii) reduce the final cost of the fuel since non-edible feed stock is typically cheaper, (iii) recycle waste, (iv) burning biodiesel does not contribute to net atmospheric carbon dioxide levels, and (v) produced fuel is biodegradable. Production of biodiesel also has its disadvantages. Transesterification is normally achieved using alkaline catalysts. These catalysts are corrosive and form unwanted by-products that are expensive to separate. Homogenous acid catalysts can also be used, but these are difficult to recycle, operate at high temperatures, and have significant corrosion and environmental issues.

Catalytic Transesterification

Transesterification reactions can be catalyzed by alkalis or enzymes. The catalytic transesterification of vegetable oils with methanol is an important industrial method used in biodiesel synthesis.

Also known as methanolysis, this reaction is well studied and established using acids or alkalis, such as sulfuric acid or sodium hydroxide as catalysts. However, these catalytic systems are less active or completely inactive for long chain alcohols. Usually, industries use sodium or potassium hydroxide or sodium methoxide or potassium methoxide as a catalyst since they are relatively cheap and quite active for this reaction. Enzyme-catalyzed procedures, using lipase as a catalyst, do not produce side reactions, but the lipases are expensive for industrial-scale production and a three-step process was required to achieve a 95% conversion.

The acid-catalyzed process is useful when a high amount of free acids is present in the vegetable oil, but the reaction time is long (48 to 96 hours), even at the boiling point of the alcohol, and a high molar ratio of alcohol is needed (20:1 wt/wt to the oil).

The transesterification process is catalyzed by alkaline metal alkoxides, and hydroxides, as well as sodium or potassium carbonates. Alkali-catalyzed transesterification with short-chain alcohols, for example, generates high yields of methyl esters in short reaction times. The alkaline catalysts show high performance for obtaining vegetable oils with high quality, but a question often arises; that is, the oils contain significant amounts of free fatty acids which cannot be converted into biodiesels but to a lot of soap. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water.

Triglycerides are readily transesterified in a batch operation in the presence of alkaline catalyst at an atmospheric pressure and at a temperature of approximately 60 to 70°C (140 to 158°F) with an excess of methanol. It often takes at least several hours to ensure the alkali (NaOH or KOH) catalytic transesterification reaction is complete. Moreover, removal of these catalysts is technically difficult and brings extra cost to the final product. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts since they produce high yields (>98%) in short reaction times (30 minutes) even if they are applied at low molar concentrations (0.5 mol%).

The transesterification process is catalyzed by sulfuric, hydrochloric, and organic sulfonic acids. In general, acid-catalyzed reactions are performed at high alcohol-to-oil molar ratios, low-to-moderate temperatures and

pressures, and high acid catalyst concentrations. These catalysts produce high yields in alkyl esters, but these reactions are slow, requiring typically temperature above 100°C (212°F) and more than 3 h to complete the conversion.

Enzyme (such as lipase)-catalyzed reactions have advantages over traditional chemical-catalyzed reactions: the generation of no by-products, easy product recovery, mild reaction conditions, and catalyst recycling. Also, enzymatic reactions are insensitive to free fatty acids and water content in waste cooking oil. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems. The enzyme reactions are highly specific and chemically clean. Because the alcohol can be inhibitory to the enzyme, a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. The reactions are slow, with a three-step sequence requiring from 4 to 40 h, or more. The reaction conditions are modest, from 35 to 45°C (85 to 115°F). The main problem of the enzyme-catalyzed process is the high cost of the lipases used as a catalyst.

Synthesis of biodiesel using enzymes such as *Candida antarctica*, *Candida rugosa*, *Pseudomonas cepacia*, immobilized lipase (Lipozyme RMIM), *Pseudomonas* sp., and *Rhizomucor miehei* is reported in the literature. The best yield 98% (w/w) was obtained by using *Pseudomonas cepacia* lipase immobilized on celite at 50°C (122°F) in the presence of 4 to 5% w/w water in 8 hours.

Process Parameters

The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time, and the contents of free fatty acids and water in oils.

The free fatty acids and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. In the transesterification, free fatty acids and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst, and reduces catalyst effectiveness, all of which result in a low conversion. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water. To carry the base-catalyzed reaction to completion, a free fatty acid value lower than 3% is needed.

The presence of water has a greater negative effect on transesterification than that of the free fatty acids. In the transesterification of beef tallow catalyzed by sodium hydroxide (NaOH) in the presence of free fatty acids and water, the water and free fatty acid contents must be maintained at specified levels.

Transesterification can occur in different temperatures depending on the type of oil employed. The conversion rate increases with reaction time. The transesterification of rice bran oil with methanol was studied at molar ratios of 4:1, 5:1, and 6:1. At molar ratios of 4:1 and 5:1, there was significant increase in yield when the reaction time was increased from 4 to 6 h. Among the three molar ratios studied, ratio 6:1 gave the best results.

One of the most important factors that affect the yield of ester is the molar ratio of alcohol to triglyceride. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1, higher molar ratios are used to enhance the solubility and to increase the contact between the triglyceride and alcohol molecules. In addition, investigation of the effect of molar ratio on the transesterification of sunflower oil with methanol showed that when the molar ratio varied from 6:1 to 1:1 and concluded that 98% conversion to ester was obtained at a molar ratio of 6:1.

Another important variable affecting the yield of methyl ester is the type of alcohol to triglyceride. Short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields.

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, and enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially, and, quite often, for the base-catalyzed transesterification, the best yields were obtained when the catalyst was used in a small concentration, i.e., 0.5% wt/wt of oil. On the other hand, data show that during the production of free and bound ethyl ester (FAEE) from castor oil, hydrochloric acid is much more effective than sodium hydroxide at higher reaction temperatures.

See also: Biodiesel, Esterification, Transesterification.

Supercritical Methanol Process

The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol, and butanol has proved to be the most promising process. Recently, a catalyst-free method was developed for biodiesel production by

employing supercritical methanol. The supercritical treatment at 350°C (650°F) and approximately 6,000 psi with a molar ratio of 42 in methanol is the optimum condition for transesterification of oil from rapeseed to biodiesel fuel.

To achieve more moderate reaction conditions, further effort was made through the two-step preparation. In this method, oils/fats are, first, treated in subcritical water for hydrolysis reaction to produce fatty acids. After hydrolysis, the reaction mixture is separated into oil phase and water phase by decantation. The oil phase (upper portion) is mainly fatty acids, while the water phase (lower portion) contains glycerol in water. The separated oil phase is then mixed with methanol and treated at supercritical condition to produce FAME thorough methyl esterification. After removing unreacted methanol and water produced in reaction, FAME can be obtained as biodiesel. Therefore, in this process, methyl esterification is the main reaction for FAME formation, while in the one-step method, transesterification is the major one.

Reaction by supercritical methanol has some advantages which are (i) glycerides and free fatty acids are reacted with equivalent rates, (ii) the homogeneous phase eliminates diffusive problems, (iii) the process tolerates great percentages of water in the feedstock catalytic process require the periodical removal of water in the feedstock or in intermediate stage to prevent catalyst deactivation, (iv) the catalyst removal step is eliminated, and (v) if high methanol/oil ratios are used, total conversion of the oil to the product can be achieved in a few minutes.

Some disadvantages of the one-stage supercritical method are clear and are (i) the process operates at high pressures, (ii) the high temperatures used in the process require proportionally high heating and cooling costs, (iii) the high methanol/oil ratios which are typically set at 42 involve high costs for the evaporation of the unreacted methanol, and (iv) the process as proposed to date does not explain how to reduce free glycerol to less than 0.02% as established in a variety of international standards.

See also: Biodiesel, Esterification.

Transformation in the Environment

The major groups of pollutants and the principal reactions that can occur when the pollutants are released into the environment (degradation reactions or transformation reactions) require (i) the knowledge of the type of pollutants and (ii) the reactivity of the pollutants so that the design of the relevant method to remove the pollutants from the environment can be achieved. Although much emphasis has been, and continues to be, placed on biotic reactions carried out by the various biota (such as bacteria), important transformation reactions of the pollutants in the environment must not be omitted. Some of these chemical reactions will be beneficial – in terms of pollutant removal – while other chemical reactions may have adverse effects on pollutant removal by converting the pollutant to a product that is more capable of remaining in the environment and may even prove to be a persistent chemical. Thus, emphasis must be placed on the occurrence of partial degradation of pollutants and the role of the intermediate products that are toxic to floral and faunal organisms, inhibit further degradation, or have adverse effects on the environment. Thus, the chemical transformation of an chemical contaminant in the environment is an issue that needs to be given serious consideration because of the changes (often non-benign) that can occur to the chemical (Manzetti et al., 2014). It would be unusual if the chemical transformation did not show some effect on the properties of the discharged chemical.

The, chemical transformations of chemicals released into the environment are, in the context of this book, considered to be the transformation of the released chemical into a product that is still of concern in terms of toxicity. Furthermore, knowledge of the relative amounts of each species present is critical because of the potential for differences in behavior and toxicity (including the possibility of enhanced toxicity) which are of concern because of the potential fate of such chemicals.

As used here, the term *fate* refers to the ultimate disposition of the chemical in the ecosystem, either by chemical or biological transformation to a new form which (hopefully) is non-toxic (degradation) or, in the case of ultimately persistent pollutants, by conversion to less offensive chemicals or even by sequestration in a sediment or other location which is expected to remain undisturbed. Thus latter option – the sequestration in a sediment or other location – is not a viable option as for safety reasons, the chemical must be dealt with at some stage of its environmental life cycle and the chemical is likely to manifest its presence at some future date.

Furthermore, chemicals released into the environment are subject to two processes that determine the fate of the chemical in the environment: (i) the potential for transportation of the chemical and (ii) the chemical changes that can occur once the chemical has been released to the environment and which depend upon the chemical properties that can affect transportation processes and physical properties that can play a role in the transformation processes.

In the present context, when a chemical (or a mixture of chemicals) is released into the environment, the issues that need to be considered are (i) the toxicity of the chemical, (ii) the concentration of the released chemical, (iii) the concentration of the toxic chemical in the released material, (iv) the potential of the chemical to migrate to other sites, (v) the potential of the chemical to produce a toxic degradation product, whether or not the toxicity is lower or higher than the toxicity of the released chemical, (vi) the potential of the toxic degradation product or products to migrate to other sites, (vii) the persistence of the chemical in an ecosystem, (viii) the persistence of any toxic degradation product in an ecosystem, (ix) the potential for the toxic degradation product to degrade even further into harmful or non-harmful constituents and the rate of degradation, and (x) the degree to which the constituent or any degradation product of the constituent can accumulate in an ecosystem,

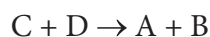
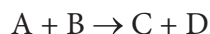
In order to complete such a list and monitor the behavior and effects of chemicals in an ecosystem, an understanding of chemical transformation processes in which a disposed or discharged chemical might particulate is valuable to any study of the effects on the environment. Chemical transformation processes change the chemical composition and structure of the discharged chemical which can change the properties (and possibly the toxicity) of the chemical and influence the behavior and life-cycle of the chemical in the environment.

As an example of chemical transformation of chemicals in the environment, weathering processes are ever-present and include such phenomena as (i) evaporation, (ii) leaching, which is transferred to the aqueous phase through dissolution, (iii) entrainment, which physical transport along with the aqueous phase, (iv) chemical oxidation, and (v) microbial degradation. The rate of transformation of the chemical is highly dependent on environmental conditions. For example, a product such a low-boiling naphtha solvent (boiling range 30 to 90°C, 86 to 194°F – a mixture of hydrocarbon derivatives produced from crude oil – will evaporate readily when spilled on to the surface of the Earth (specifically a water surface or land surface) and will give the appearance of a reception in the amount that remains. But the low-boiling constituents have not merely *disappeared* or *gone away* but have transferred from the land or from the water into the atmosphere. On the other hand, naphtha that has been inadvertently released into a formation that lies below a formation of clay minerals will tend to evaporate slowly (the clay can act as a formation trap) and may not be readily detectable.

However, the various chemical transformation processes, which influence the presence and the analysis of chemicals at a particular site, although often represented by simple (and convenient) chemical equations, can be complex (Neilson and Allard, 2012), and the true nature of the chemical transformation process is difficult to elucidate. The extent of transformation is dependent on many factors including (i) the properties of the chemical, (ii) the geology of the site, (iii) the climatic conditions, such as temperature, oxygen levels, and moisture, (iv) the type of microorganisms present, and (v) any other environmental conditions that can influence the life-cycle of the chemical. In fact, the primary factor controlling the extent of chemical transformation is the molecular composition of the chemical contaminant.

In the environment, a chemical transformation is the same principle as in the laboratory or in the chemical process industries – the transformation of a substrate to a product – but whether or not the product is benign and less likely to harm the environment (relative to the substrate) or is more detrimental by exerting having a greater impact on the environment depends upon the origin, properties, and reactivity pathways of the starting substrate. Thus, a chemical transformation requires a chemical reaction to lead to the transformation of one chemical to another (Neilson and Allard, 2012).

Transformation reactions may proceed in the forward direction and processed to completion as well as in the reverse direction until they reach equilibrium.



Thus,



Reactions that proceed in the forward direction to approach equilibrium are often described as spontaneous, requiring no input of free energy to go forward. Non-spontaneous reactions require input of free energy to go forward (examples application of heat for the reaction to proceed). In chemical synthesis, different chemical reactions are used in combinations during chemical synthesis in order to obtain a desired product. Also, in chemistry, a consecutive series of chemical reactions (where the product of one reaction is the reactant of the next reaction) are often catalyzed by a variety of catalysts which increase the rates of biochemical reactions, so that syntheses and decompositions impossible under ordinary conditions can occur at the temperatures, pressures, and reactant concentrations present within a reactor and, by inference, within the environment.



This simplified equation illustrates the potential complexity of chemical reaction, and such complexity must be anticipated when a chemical is transformed in an environmental ecosystem.

Thus, the focus is to develop a fundamental understanding of the nature of the chemical processes that occur when inorganic chemicals or organic chemicals are released into the environment. With this information, the activities that have an effect on the environment the chemistry can be estimated and even predicted.

See also:

Transuranium Elements

The transuranium elements (also known as transuranic elements) are the chemical elements with atomic numbers greater than 92, which is the atomic number of uranium (Table T-2). All of these elements are unstable and undergo radioactive decay into other elements.

Table T-2 The Periodic Table of the Elements.

1 H																	2 He				
3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg															13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
37 Rb	38 Sr	Y	72 Zr	73 Nb	74 Mo	75 Tc	76 Ru	77 Rh	78 Pd	79 Ag	80 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn				
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118				
						57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
						89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Of the elements with atomic numbers 1 to 92, most can be found in nature, having stable isotopes (such as hydrogen) or long-lived radioisotopes (such as uranium), or existing as common products of the decay of uranium and thorium (such as radon). The exceptions are elements 43, 61, 85, and 87 – all of which occur in nature.

Trace amounts of neptunium and plutonium form in some uranium-rich rock, and small amounts are produced during atmospheric tests of nuclear weapons. These two elements are generated from neutron capture ore with subsequent beta decay. Thus:



A beta particle has a small mass and is usually negatively charged. It is emitted from the nucleus of an atom with a charge of minus one. Beta radiation causes ionization by interfering with electrons in their orbits. Both have a negative charge, so the electrons are repelled when the beta particle passes.

All of the elements with a higher atomic number than plutonium (atomic number = 94) are synthetic insofar as they are created in nuclear reactors or particle accelerators. The half-life of each of these elements shows a general trend of decreasing as atomic number increases. There are exceptions, however, including several isotopes of curium (Cm, atomic number = 96) and dubium (Db, atomic number = 105). Some elements in this series (atomic numbers 110 to 114) are thought to break the trend and demonstrate increased nuclear stability, comprising the theoretical island of stability.

See also: Radioactive Decay.

Traveling Grate Furnace

The traveling grate furnace is a type of furnace in which assembled links of grates are joined together in a perpetual belt arrangement and, thus, the traveling grate is a wide steel belt that carries the feedstock through the furnace. More specifically, the traveling grate is comprised of chain that carries the pellets like a conveyor. The difference is that the grate chain allows air to pass through it. The grate chain travels flat and straight, and in operation, fuel is fed in at one end and ash is discharged at the other.

While on the traveling grate, hot air is blown through the bed to dry and preheat the feedstock (usually pelletized) in preparation for being discharged into a rotary kiln. The pellets undergo an oxidation-reduction reaction in the kiln resulting in a change of chemistry and a hardened product suitable for transport to and use in blast furnaces.

The thickness of the bed in the traveling grate must remain consistent, despite fluctuations in the feed rate from upstream equipment, to maintain constant performance from the rotary kiln and maintain chemistry for the furnace.

See also: Combustion.

Tritium

Tritium (hydrogen-3) is the only radioactive isotope of hydrogen. The nucleus of a tritium atom consists of a proton and two neutrons. This contrasts with the nucleus of an ordinary hydrogen atom (which consists solely of a proton) and a deuterium atom (which consists of one proton and one neutron) (Table T-3).

Table T-3 The isotopes of hydrogen.

Isotope	Description
Protium	Ordinary hydrogen with one proton and one electron in the atom. When two atoms of protium are combined with one atom of oxygen, water is created.
Deuterium	Sometimes called "heavy hydrogen," a non-radioactive isotope that has a neutron in the atom, in addition to the proton and electron. Water made with this isotope is called "heavy water."
Tritium	A radioactive isotope of hydrogen that has two neutrons in addition to the proton and the electron. Water made with this isotope is called tritium oxide. Tritium is the only one of the three hydrogen isotopes that is radioactive.

Ordinary hydrogen comprises over 99.9% of all naturally occurring hydrogen. Deuterium comprises approximately 0.02%, and tritium comprises approximately a billionth of a billionth (10^{-18}) percent.

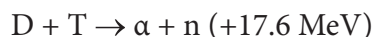
The most common forms of tritium are tritium gas (HT) and tritium oxide, also called “tritiated water.” In tritiated water, a tritium atom replaces one of the hydrogen atoms so the chemical form is HTO (hydrogen-tritium-oxygen) rather than H_2O (hydrogen-hydrogen-oxygen). The chemical properties of tritium are essentially the same as those of ordinary hydrogen. It decays with a half-life of 12 years by emitting a beta particle to produce helium-3. Tritium has a relatively high specific activity and is generated by both natural and artificial processes.

Tritium is naturally present as a small percentage of ordinary hydrogen in water, both liquid and vapor. This tritium is produced as a result of the interaction of cosmic radiation with gases in the upper atmosphere. After being produced in the atmosphere, tritium is readily incorporated into water and falls to earth as rain, thus entering the natural hydrological cycle.

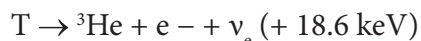
Tritium is also produced as a fission product in nuclear weapons tests and in nuclear power reactors, with a yield of approximately 0.01%. That is, approximately one atom of tritium is produced per 10,000 fissions. Because little tritium is naturally present, it must be produced artificially for use on a practical scale. Tritium can be made in production nuclear reactors, i.e., reactors designed to optimize the generation of tritium and special nuclear materials such as plutonium-239. Tritium is produced by the neutron absorption of a lithium-6 atom. The lithium-6 atom, with three protons and three neutrons, and the absorbed neutron combine to form a lithium-7 atom with three protons and four neutrons, which instantaneously splits to form an atom of tritium (one proton and two neutrons) and an atom of helium-4 (two protons and two neutrons).

While tritium can also be produced in accelerators by bombarding helium-3 with neutrons, this approach has not been proven on a large scale. How is it used? Tritium is used as a component in nuclear weapons to boost the yield of both fission and thermonuclear (or fusion) warheads. Tritium is also used as a tracer in biological and environmental tritium (hydrogen-3).

The first generation of controlled fusion devices are being designed to liberate heat from the fusion of a deuteron (D) and a triton (T) to form an alpha particle, α , and a neutron, n, in the strongly exothermic nuclear reaction:



Radioactive tritium spontaneously decays to ^3He , an electron e^- and an electron antineutrino ($\bar{\nu}_e$) with a half-life of 12.3 years in the process of beta-decay:



The stable isotope ^3He , produced when tritium decays, has many uses already, for example, in neutron detectors, in ^3He - ^4He dilution refrigerators to produce millikelvin temperatures, and in magnetic-resonance imaging. Naturally occurring ^3He is so rare that virtually all of the current demand for ^3He is met with gas collected from the radioactive decay of tritium. In fact, tritium breeding is an essential component of potential future sources of electrical energy based on nuclear fusion.

See also: Deuterium, Hydrogen, Protium, Nuclear Fission, Nuclear Fusion.

Troposphere

The troposphere forms the bottom-most layer of the homosphere and is thus closest to the surface of the Earth – which is the layer of the atmosphere where life can exist without artificial life-support systems. It is also known as the weather layer of the Earth as it has all weather conditions. Airplanes fly at the very top of the troposphere, so they can fly over the weather, which causes turbulence. The jet stream, a fast-moving region of wind in the upper troposphere has been estimated to be on the order of 300 miles (or more) per hour. While temperatures at the bottom of the troposphere are nice and hospitable for life, temperatures at the top are approximately -50°C (-60°F). The troposphere is also the thinnest layer of the atmosphere and is approximately 10 miles high.

Thus, the troposphere is lowest layer of the atmosphere extending from sea level to an altitude of approximately 635 miles is the troposphere, which is characterized by a generally homogeneous composition of major gases other than water and decreasing temperature with increasing altitude from the heat-radiating surface of the land. The upper limit of the troposphere, which has a temperature minimum of approximately -56°C (-69°F), varies in altitude by a half mile (a kilometer) or so with atmospheric temperature, underlying terrestrial surface, and time. The homogeneous composition of the troposphere results from constant mixing by circulating air masses. However, the water vapor content of the troposphere is extremely variable because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies. The boundary between the troposphere and the overlying stratosphere is known as the tropopause.

The troposphere contains the weather systems, air pollution, and the bulk of volcanic gases. The layer is characterized by air temperatures that decrease upward as distance increases from the warm surface of the Earth. Since the layer is defined by its thermal character, it would be expected to be thicker above warm regions and thinner over cold areas. In fact, the thickness of the troposphere increases from 5 miles over the polar regions of the Earth to as much as 10 miles at the equator.

See also: Atmosphere.

Tumbling-Bed Gasifier

The tumbling bed gasifier is an apparatus in which the feedstock is lifted vertically in a revolving cylinder and dropped through an axially flowing stream of oxygen and steam.

See also: Gasification, gasifiers.

Turbine

A turbine is a rotary mechanical device that extracts energy from a fluid flow and converts the energy into useful work. The work produced by a turbine can be used for generating electrical power when combined with a generator. A turbine is a turbomachine with at least one moving part (a rotor assembly) which is a shaft or drum with blades attached. Moving fluid acts on the blades so that they move and impart rotational energy to the rotor. Early examples of turbines are windmills and waterwheels.

Gas, steam, and water turbines have a casing around the blades that contains and controls the working fluid. Modern steam turbines frequently employ both reaction and impulse in the same unit, typically varying the degree of reaction and impulse from the blade root to its periphery.

In practice, modern turbine designs use both reaction and impulse concepts to varying degrees whenever possible. Wind turbines use an airfoil to generate a reaction lift from the moving fluid and impart it to the rotor. Wind turbines also gain some energy from the impulse of the wind, by deflecting it at an angle. Turbines with multiple stages may use either reaction or impulse blading at high pressure. Steam turbines were traditionally more impulse but continue to move toward reaction designs similar to those used in gas turbines. At low pressure, the operating fluid medium expands in volume for small reductions in pressure. Under these conditions, blading becomes strictly a reaction-type design with the base of the blade solely impulse due to the effect of the rotation speed for each blade. As the volume increases, the blade height increases, and the base of the blade spins at a slower speed relative to the tip. This change in speed forces a designer to change from impulse at the base, to a high reaction-style tip.

See also: Steam Turbine.

Turbine - Condensing

The condensing turbine is able to use the total energy of the inlet steam flow to a maximum extent. Therefore, this type of turbine is used for power utilities that want to supply electricity to consumers as much as possible.

The last stages of a large condensing turbine operate in the wet steam region, where the steam contains 5 to 12% w/w water. Erosion of the turbine blades is initiated by a relatively small proportion of the water droplets in the steam separating out and collecting on the concave pressure face of the diaphragm blades, where a film is formed which is drawn toward the trailing edge by the drag of the steam. Here, the film grows and passes around the trailing edge on to the convex face where, usually in a region of strong secondary flow, droplets move back and forth increasing in size until they are torn away by the shearing action of the main flow of steam. Relatively large drops (50-200 μm in diameter) are produced and have to be accelerated from rest by the steam. These large drops arrive at the inlet plane of the moving blade row at only a fraction of the absolute velocity of the steam and are subsequently struck by the convex surfaces of the moving blade row.

The condensing turbine has heat discharge loss because all exhaust steam flow is condensed in the condenser that is cooled by cooling water, which means that a lot of discharged heat is thrown away outside. Furthermore, the condensing turbine consists of many turbine stages and large steam flow in the low pressure turbine; as a result, the low pressure turbine will become larger.

See also: Horizontal and Vertical Axis Turbine, Turbine.

Turbine – Horizontal and Vertical Axis

Both horizontal and vertical axis turbines are applicable to applications such as tidal currents or river streams and are perceived as a critical element to hydrokinetic conversion concepts. Hydrokinetic energy conversion may employ either rotary turbo machinery or can use non-turbine schemes. While the former class (turbine system) encompasses various classical rotary technologies, the latter group (non-turbine system) is mostly based on various unconventional concepts. Such schemes include oscillating hydrofoil [30], vortex- induced vibration, piezo polymer conversion, and variable geometry sails.

See also: Horizontal and Vertical Axis Turbine, Turbine.

Turbine – Impulse

Impulse turbines or turbine stages are simple, single-rotor or multirotor (compounded) turbines to which impulse blades are attached. Impulse blades can be recognized by their shape. Because they are usually used in the entrance high-pressure stages of a steam turbine, when the specific volume of steam is low and requires much smaller flow areas than at lower pressures, the impulse blades are short and have constant cross sections. Impulse turbines are also characterized by the fact that most or all of the enthalpy and hence the pressure drop occurs in the nozzles (or fixed blades that act as nozzles) and little or none in the moving blades.

An impulse turbine changes the direction of flow of a high velocity fluid or gas jet. The resulting impulse spins the turbine and leaves the fluid flow with diminished kinetic energy. There is no pressure change of the fluid or gas in the turbine blades (the moving blades), as in the case of a steam or gas turbine; all the pressure drop takes place in the stationary blades (the nozzles). Before reaching the turbine, the pressure head of the fluid is changed to velocity head by accelerating the fluid with a nozzle. Pelton wheels and de Laval turbines use this process exclusively. Impulse turbines do not require a pressure casing around the rotor since the fluid jet is created by the nozzle prior to reaching the blades on the rotor. Newton's second law describes the transfer of energy for impulse turbines. Impulse turbines are most efficient for use in cases where the flow is low and the inlet pressure is high.

See also: Turbine.

Turbine – Reaction

A reaction turbine develops torque by reacting to the gas or fluid's pressure or mass. The pressure of the gas or fluid changes as it passes through the turbine rotor blades. A pressure casing is needed to contain the working fluid as it acts on the turbine stage(s), or the turbine must be fully immersed in the fluid flow (such as with wind turbines).

The casing contains and directs the working fluid and, for water turbines, maintains the suction imparted by the draft tube. A Francis turbine and most steam turbines use this concept. For compressible working fluids, multiple turbine stages are usually used to harness the expanding gas efficiently. Newton's third law describes the transfer of energy for reaction turbines. Reaction turbines are better suited to higher flow velocities or applications where the fluid head (upstream pressure) is low.

See also: Turbine.

Turbine – Steam

The steam turbine is a device that extracts thermal energy from pressurized steam and uses it to do mechanical work on a rotating output shaft. It is a form of heat engine that derives much of its improvement in thermodynamic efficiency from the use of multiple stages in the expansion of the steam, which results in a closer approach to the ideal reversible expansion process. Because the turbine generates rotary motion, it is particularly suited to be used to drive an electrical generator.

In the case of steam turbines, such as would be used for marine applications or for land-based electricity generation, a Parsons-type reaction turbine would require approximately double the number of blade rows as a de Laval-type impulse turbine, for the same degree of thermal energy conversion. While this makes the Parsons turbine much longer and heavier, the overall efficiency of a reaction turbine is slightly higher than the equivalent impulse turbine for the same thermal energy conversion.

See also: Electricity Generation – Equipment, Steam Turbine.

Turbopause

The turbopause (also known as the homopause) marks the altitude in an atmosphere below which turbulent mixing dominates. The region below the turbopause (the homosphere) is the region in which the atmosphere is well mixed for chemical species which have long mean residence times. Highly reactive chemicals tend to have variable concentration throughout the atmosphere, while unreactive species have more homogeneous concentrations. The region above the turbopause is the heterosphere, where molecular diffusion dominates and the chemical composition of the atmosphere varies according to chemical species and their atomic weight.

Turbulence plays an important role through much of the atmosphere of the Earth. Below a height of approximately 65 miles, turbulence mixes the various species of gas that make up the atmosphere. As a result of this mixing, the major gases are found in approximately the same proportion just below 60 miles as they are at the ground. This region is called the heterosphere. The boundary below which there is mixing of all species, the homopause, is in fact somewhat lower than the turbopause, the height above which no turbulence occurs. This difference in altitude exists because less turbulence occurs in the highest parts of the turbulent region and mixing is not as complete. The turbopause itself exists because it represents the lower boundary of a region in which molecular viscosity and ion drag damp vertical gradients to such an extent that the small structures associated with turbulence are not formed. Thus, there is no process that mixes the gas and maintains the same composition throughout the rest of the thermosphere. Instead, the density of each species decreases with altitude above the turbopause at a rate that is related to the mass of the species.

See also: Atmosphere.

Two-Stage Gasification

The two-stage gasification process is a process in which partial gasification or pyrolysis is the first step followed by complete gasification of the resultant char in a second step.

The major methods of biomass thermal conversion are (i) combustion in excess oxygen, (ii) gasification in reduced oxygen, and (iii) pyrolysis in the absence of oxygen, and the end products of these methods are heat, gas, liquid, and solid fuels. However, in terms of energy production, these methods are not always optimal.

A two-stage thermal conversion of biomass based on pyrolysis as the first stage and pyrolysis products cracking as the second stage can be considered the optimal method for energy production that allows obtaining synthesis gas consisting of hydrogen and carbon monoxide and not containing liquid or solid particles.

The E-Gas process features a two-stage gasifier design in which the gasifier is refractory-lined and uses coal-water slurry feed. The first stage of the gasifier has two opposed, horizontally oriented feed injectors. The synthesis gas exits the top of the first stage, and slag flows out of the bottom into a water bath. The synthesis gas produced by the first stage enters the second stage at temperatures comparable to the exit temperatures of the other two entrained flow gasifiers. Additional coal-water slurry is injected into this hot syngas in the second gasifier stage, but no additional oxygen is injected. Endothermic gasification reactions occur between the hot syngas and the second stage coal feed. This lowers the temperature of the syngas and increases the cold gas efficiency of the process. Upon exiting the top of the second stage of the gasifier, the syngas passes through a syngas cooler which features a firetube design. The cooled syngas then enters a rigid barrier filter where any unconverted char from the second stage is collected and recycled back to the first stage of the gasifier where the hotter temperatures ensure near complete carbon conversion.

The advantage of the two-stage process in comparison with air gasification is the high calorific value of gas produced due to the absence of nonflammable nitrogen in its composition. Another advantage of the process is the relatively low cost in comparison with other gasification methods, such as oxygen or steam gasification.

See also: E-Gas Process.

U-Gas Process

The U-Gas process was developed to produce gaseous product from coal in an efficient and environmentally acceptable manner. The product gas may be used to produce low-Btu gas, medium-Btu gas, and synthetic natural gas (SNG) for use as fuels, or as chemical feedstocks for the production of ammonia, methanol, hydrogen, and oxo-chemicals, or for electricity generation. The process is capable of handling large volumes of gas throughput, achieving a high conversion of coal to gas without producing tar or oil, and causing minimum damage to the environment. The process is based on a single-stage, fluidized bed gasifier which accomplishes four principal functions in a single stage, which are (i) decaking coal, (ii) devolatilizing coal, (iii) gasifying coal, and (iv) agglomerating and separating ash from char.

In the process, coal of approximately 0.25-inch diameter is dried and pneumatically injected into the gasifier through a lock hopper system. In the fluidized bed reactor, coal reacts with steam and oxygen at a temperature of 950 to 1,100°C (1,740 to 2,010°F). The temperature of the bed is determined based on the type of coal feed and is controlled to prevent slagging conditions of ash. The pressure typically ranges from 50 to 350 psi, and is largely determined based on the ultimate use of the final product gas. Oxygen may be substituted with air.

In the gasifier, coal is rapidly gasified producing hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and small amounts of methane (CH_4). The fluidized bed is always maintained under reducing conditions, and, as such, all sulfur species present in coal is converted into hydrogen sulfide (H_2S). During the process, the ash is agglomerated into spherical particles that grow in size and are separated from the bed into water-filled ash hoppers, from which they are withdrawn as slurry. A portion of fluidizing gas enters the gasifier section through an inclined grid, whereas most of the remaining entering gas flows upward at a high velocity through the ash-agglomerating zone and forms a relatively hot zone within the bed.

Coal fines elutriated from the bed are collected by two external cyclones – the fines from the first cyclone are returned to the bed, whereas the fines from the second cyclone are sent to the ash-agglomerating zone. Raw product gas is virtually free of tar and oils, thus simplifying the ensuing energy recovery and gas purification steps.

See also: Gasification.

Ultrafiltration and Microfiltration

The ultrafiltration process and the microfiltration process are pressure-driven filtration processes in which the smaller pores of the ultrafiltration membranes make the retention of large dissolved species (typically with a molecular weight greater than 500) along with retention of any particulate matter. Thus, the distinction between ultrafiltration and microfiltration is made on the basis of the size of the materials screened out by the membrane and thus on the apparent size of the holes in the membrane.

The range of pore sizes described for ultrafiltration membranes is typically on the order of 20 to 1,000 Å, while microfiltration membranes have pores in the range of 1,000 to 100,000 Å (0.1 to 10 microns). These pore size ranges describe what is meant by ultrafiltration and microfiltration membranes.

The membranes for microfiltration can be either of two main types having different pore structures. One type consists of a relatively thick spongy structure of polymer much like the support layer of a reverse osmosis membrane. It has tortuous pores through the membrane with a relatively wide size distribution. Furthermore, the pore diameter can vary along the pore length. Thus, plugging of the pores can be a problem if the pores are too close to the size of the particles to be rejected. The other type of membrane has a narrow size distribution of straight-through pores. It is usually much thinner than the spongy membrane.

Because of the higher molecular weights of the solutes removed by ultrafiltration as compared to reverse osmosis, osmotic pressure is low enough not to be a consideration. Generally, pressure gradients as low as 5 to 100 psig across the membrane are sufficient to achieve satisfactory flux rates. Furthermore, the larger pore size in ultrafiltration membranes can lead to passage of ionic materials and small molecules, while retaining larger dissolved organic species. These retained substances may be insoluble particulate matter such as complexed heavy metals and other suspended solids.

See also: Membrane Permeation, Membrane Processes.

Unconventional Gas

Unconventional gas is gas that occurs in tight sandstones, siltstones, sandy carbonates, limestone, dolomite, and chalk. The boundary between conventional gas and unconventional gas resources is not well defined, because they result from a continuum of geologic conditions. Coal seam gas, more frequently called coal bed methane, is frequently referred to as unconventional gas. Tight shale gas and gas hydrates are also placed into the category of unconventional gas.

One form of unconventional gas is coal bed methane (CBM) which is the generic term given to methane gas held in underground coal seams and released or produced when the water pressure within the seam is reduced by pumping from either vertical or inclined to horizontal surface holes. The methane is predominantly formed during the coalification process whereby organic matter is slowly transformed into coal by increasing temperature and pressure as the organic matter is buried deeper and deeper by additional deposits of organic and inorganic matter over long periods of geological time. This is referred to as thermogenic coal bed methane.

Shale gas is another form of unconventional gas, and large continuous gas accumulations are sometimes present in low permeability shale, (tight) sandstones, siltstones, sandy carbonates, limestone, dolomite, and chalk. Such gas deposits are commonly classified as unconventional because their reservoir characteristics differ from conventional reservoirs and they require stimulation to be produced economically.

Gas hydrates are another form of unconventional gas and are molecules consisting of an ice lattice or cage in which low-molecular-weight hydrocarbon derivatives, such as methane, are embedded. The two major conditions that promote hydrate formation are: (1) high gas pressure and low gas temperature and (2) the gas at or below its water dew point with free water present.

Gas hydrates are common constituents of the shallow marine geosphere and occur both in deep sedimentary structures, and as outcrops on the ocean floor. Methane hydrates are believed to form by migration of gas from depth along geological faults, followed by precipitation, or crystallization, on contact of the rising gas stream with cold sea water. At high pressures, methane hydrates remain stable at temperatures up to 18°C and the typical methane hydrate contains one molecule of methane for every 6 molecules of water that forms the ice cage, but this ratio is dependent on the number of methane molecules that fit into the various cage structures of the water lattice. One liter of solid methane hydrate can contain up to 168 liters of methane gas.

Undiscovered Reserves

One major issue in the estimation of coal (or for that matter any fossil fuel or mineral) resource is the all-too-frequent use of the term *undiscovered resources* (Table U-1). Often, the data provided to substantiate such reserves are very speculative and open to questions related to the degree of certainty. There are three important items that counteract the guesswork applied to *undiscovered* resources: (i) the actual discoveries of new coal reserves, (ii) the development of improved mining technologies for already known coal reserves, and (iii) estimates of the coal resource base that are derived from known resource properties where the whole of the resource is not explored.

Table U-1 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

The total resource base of any fossil fuel (or, for that matter, of any mineral resource) will be dictated by economics. When coal resource data are quoted, some attention must be given to the cost of recovering those reserves. Most importantly, the economics must also include a cost factor that reflects the willingness to secure total, or a specific degree of, energy independence, including some serious consideration of the very real environmental aspects of coal use.

See also: Reserves.

Unit Process

A unit process (sometimes referred to as a unit operation) is a basic physical operation in a processing sequence. Examples are distillation, absorption, fluid flow, as well as heat and mass transfer. Fundamentals pertaining to a given unit operation are the same regardless of the industrial applications. Examples are: (i) fluid flow, which deals with the principles governing the flow and transportation of fluids, (ii) heat transfer, which deals with the principles underlying the heat transfer by different methods, and (iii) distillation, absorption, extraction, and drying – which are also referred to as diffusional mass transfer unit operations – in which the separation of natural gas and crude oil hydrocarbons is accomplished by the transfer of molecules from one phase to the other by diffusion.

The significance of introducing the unit operation concept in understanding the processing surface operations in a natural gas field or an oil field is apparent to readers when it is realized that most of these surface operations are *physical operations processes* or *non-reacting processes*. The processes focus on the transfer and the transformation of *energy*, and the transfer, separation, and conditioning (treating) of *materials* by physical means.

Three modes of transfer that take place in oil field processing operations are recognized as follows: (i) momentum transfer, which is achieved by fluid flow, (ii) heat transfer of crude oil and crude oil products using heat exchangers and furnaces, and (iii) mass transfer in distillation columns, absorbers, and others that lead to enrichment and separation in which the transfer is due to the diffusion of the molecular constituents that separates the low-boiling constituents from the higher boiling constituents.

See also: Refining.

Unisol Process

The Unisol process is a regenerative chemical process for extracting mercaptan sulfur and certain nitrogen compounds from sour gasoline or distillates using regenerable aqueous solutions of sodium hydroxide or potassium hydroxide containing methanol.

More specifically, the process is a regenerative method for extracting not only mercaptan derivatives (RSH) but also certain nitrogen compounds from sour (sulfur-containing) distillates. The distillate (such as naphtha or gasoline), free of hydrogen sulfide, is washed countercurrently with aqueous caustic-methanol solution at approximately 40°C (104°F). The spent caustic is regenerated in a stripping tower (145 to 150°C, 290 to 300°F), where methanol, water, and mercaptans are removed.

Unit Collector

A unit collector, unlike a central collector, controls contamination at its source. It is small and self-contained, consisting of a fan and some form of dust collector. A unit collector is suitable for isolated, portable, or frequently moved particulate-producing (dust-producing) operations, such as bins and silos or remote belt-conveyor transfer points. The advantages of unit collectors include (i) small space requirements, (ii) the return of collected particulate matter (or dust) to main material flow, and low initial cost.

The collector is used to enhance the quality of air released from industrial and commercial processes by collecting particulate matter, dust, and other impurities from air or gas. Designed to handle high-volume loads, a collector system consists of a blower, filter, a filter-cleaning system, and a particle receptacle or particle removal system.

A number of designs are available, with capacities ranging from 200 to 2,000 ft³/min (90 to 900 L/s). There are two main types of unit collectors: (i) fabric collectors, with manual shaking or pulse-jet cleaning – normally used for fine particulate matter and dust, and (ii) cyclone collectors – normally used for coarse particulate matter and dust. Fabric collectors are frequently used in minerals processing operations because they provide high collection efficiency and uninterrupted exhaust airflow between cleaning cycles. On the other hand, cyclone collectors are used when coarser material is generated, as in woodworking, metal grinding, or machining.

See also: Centrifuge, Cyclone, Fabric Filters.

Unproven Reserves

Unproven reserves (unproved reserves) are based on geologic and/or engineering data similar to that used in estimates of proved reserves, but technical, contractual, economic, or regulatory uncertainties preclude such reserves being classified as proved (Table U-2).

Table U-2 Categorization of resources and reserves.

Resource	Undiscovered			
	Discovered	Nonrecoverable		
		Recoverable	Cumulative production	
			Reserves	Unproved
			(actual)	Probable
				Possible

In many countries, unproven reserves (due to regulatory factors or economic factors) are estimated as less recoverable and therefore unproven. This class of reserves is further broken down into subcategories of probable and possible.

See also: Resources and Reserves.

Unsaturated Hydrocarbons

The presence of olefins ($R^1CH=CHR^2$, where R^1 and R^2 can be the same or different groups) in petroleum has been under dispute for many years because there are investigators who claim that olefins are actually present. In fact, these claims usually refer to distilled fractions, and it is difficult to entirely avoid cracking during the distillation process. Nevertheless, evidence for the presence of considerable proportions of olefins in Pennsylvanian crude oils has been obtained; spectroscopic and chemical methods showed that the crude oils, as well as all distillate fractions, contained up to 3% w/w olefins. Hence, although the opinion that petroleum does not contain olefins requires some revision, it is perhaps reasonable to assume that the Pennsylvania crude oils may hold an exceptional position and that olefins are present in crude oil in only a few special cases. The presence of dienes ($RCH=CH-CH=R'$) and acetylenes ($RC\equiv CR'$) is considered to be extremely unlikely.

In summary, a variety of hydrocarbon compounds occur throughout petroleum. Although the amount of any particular hydrocarbon varies from one crude oil to another, the family from which that hydrocarbon arises is well represented.

See also: Olefin Hydrocarbons.

Updraft Combustion

Updraft combustion involves lumps of coal in a bed supported by a grate, and provision is made for the supply of primary air beneath the bed and secondary air above it as there is a connection to a flue in order to provide a draught. A fire of this type is ignited at the base, after which the flame front then spreads upward until the whole bed is incandescent. The best-known example of coal combustion is provided by the domestic fire which operates on the same over-feed principle.

See also: Combustion.

Updraft Gasifier

The simplest type of gasifier is the updraft gasifier (fixed bed countercurrent gasifier). The biomass is fed at the top of the reactor and moves downwards as a result of the conversion of the biomass and the removal of ashes. The air intake is at the bottom and the gas leaves at the top. The biomass moves in countercurrent to the gas flow, and passes through the drying zone, the distillation zone, reduction zone, and the oxidation zone.

The countercurrent fixed bed (up draft) gasifier consists of a fixed bed of carbonaceous fuel (e.g., coal or biomass) through which the "gasification agent" (steam, oxygen and/or air) flows in countercurrent configuration. The ash is either removed dry or as a slag. The slagging gasifiers require a higher ratio of steam and oxygen to carbon in order to reach temperatures higher than the ash fusion temperature. The nature of the gasifier means that the fuel must have high mechanical strength and must be non-caking so that it will form a permeable bed, although recent developments have reduced these restrictions to some extent. The throughput for this type of gasifier is relatively low. Thermal efficiency is high as the gas exit temperatures are relatively low. However, this means that tar and methane production is significant at typical operation temperatures, so the product gas must be extensively cleaned before use or recycled to the reactor.

The major advantages of this type of gasifier are its simplicity, high charcoal burn-out, and internal heat exchange leading to low gas exit temperatures and high gasification efficiency. In this way, fuels with high moisture content (up to 50% w/w) can also be used.

Major drawbacks are the high amounts of tar and pyrolysis products because the pyrolysis gas is not led through the oxidation zone. This is of minor importance if the gas is used for direct heat applications, in which the tar product is burned. In case the gas is used for engines, gas cleaning is required, resulting in problems of tar-containing condensates.

See also: Gasification, Gasifiers.

Upflow Expanded-Bed Reactor

Expanded-bed reactors are applicable to distillates, but are commercially used for very heavy, high metals, and/or dirty feedstocks having extraneous fine solids material. They operate in such a way that the catalyst is in an expanded state so that the extraneous solids pass through the catalyst bed without plugging. They are isothermal, which conveniently handles the high-temperature exotherm associated with high hydrogen consumptions. Since the catalyst is in an expanded state of motion, it is possible to treat the catalyst as a fluid and to withdraw and add the catalyst during operation.

Expanded beds of catalyst are referred to as particulate fluidized insofar as the feedstock and hydrogen flow upward through an expanded bed of catalyst with each catalyst particle in independent motion. Thus, the catalyst migrates throughout the entire reactor bed. Expanded-bed reactors are mathematically modeled as back-mix reactors with the entire catalyst bed at one uniform temperature. Spent catalyst may be withdrawn and replaced with fresh catalyst on a daily basis. Daily catalyst addition and withdrawal eliminate the need for costly shutdowns to change out catalyst and also result in a constant equilibrium catalyst activity and product quality. The catalyst is withdrawn daily and has vanadium, nickel, and carbon content that is representative on a macro-scale of what is found throughout the entire reactor. On a micro-scale, individual catalyst particles have ages from that of fresh catalyst to as old as the initial catalyst charge to the unit, but the catalyst particles of each age group are so well dispersed in the reactor that the reactor contents appear uniform.

In the unit, the feedstock and hydrogen recycle gas enter the bottom of the reactor, pass up through the expanded catalyst bed, and leave from the top of the reactor. Commercial expanded-bed reactors normally operate with 1/32 inch (0.8 mm) extrudate catalysts that provide a higher rate of desulfurization than the larger catalyst particles used in fixed-bed reactors. With extrudate catalysts of this size, the upward liquid velocity based on fresh feedstock is not sufficient to keep the catalyst particles in an expanded state. Therefore, for each part of the fresh feed, several parts of product oil are taken from the top of the reactor, recycled internally through a large vertical pipe to the bottom of the reactor, and pumped back up through the expanded catalyst bed. The amount of catalyst bed expansion is controlled by the recycle of product oil back up through the catalyst bed.

The expansion and turbulence of gas and oil passing upward through the expanded catalyst bed are sufficient to cause almost complete random motion in the bed (particulate fluidized). This effect produces the isothermal operation. It also causes almost complete back-mixing. Consequently, in order to effect near complete sulfur removal (over 75%), it is necessary to operate with two or more reactors in series. The ability to operate at a single temperature throughout the reactor or reactors, and to operate at a selected optimum temperature rather than an increasing temperature from the start to the end of the run, results in more effective use of the reactor and catalyst contents. Use of a smaller catalyst particle size, isothermal, fixed temperature throughout run, back-mixing, daily catalyst addition, and constant product quality, the reactor size required for an expanded bed is often smaller than that required for a fixed bed to achieve the same product goals.

Upper Explosive Limit

Before a fire or explosion can occur, three conditions must be met simultaneously and are (i) a fuel, such as a combustible gas, (ii) oxygen or air must exist in certain proportions, and (iii) an ignition source, such as a spark or flame. The ratio of fuel and oxygen that is required varies with each combustible gas or vapor (Table U-3).

Table U-3 Examples of the lower and upper explosive limits of selected chemicals in air.

Chemical	LEL	UEL
1,3-Butadiene	2.0	12.0
1-Butene	1.6	10.0
Benzene	1.3	7.9
Butane	1.8	8.4
Carbon Monoxide	12.5	74.0
Carbonyl Sulfide	12.0	29.0
Cyclohexane	1.3	7.8
Cyclopropane	2.4	10.4
Dimethyl Ether	3.4	27.0
Ethane	3.0	12.4
Ethanol	3.3	19.0
Ethylene	2.7	36.0
Heptane	1.1	6.7
Hexane	1.2	7.4
Hydrogen	4.0	75.0
Hydrogen sulfide	4.0	44.0
Isobutane	1.8	8.4
Isobutylene	1.8	9.6
Methane	5.0	15.0
Methanol	6.7	36.0
Methyl mercaptan	3.9	21.8
Propylene	2.4	11.0
Toluene	1.2	7.1
Xylene	1.1	6.6

The minimum concentration of a particular combustible gas or vapor necessary to support its combustion in air is the lower explosive limit (LEL) for that gas. Below this level, the mixture is too “lean” to burn. The maximum concentration of a gas or vapor that will burn in air is defined as the upper explosive limit (UEL). Above this level, the mixture is too “rich” to burn. The range between the lower explosive limit and the upper explosive limit is known as the flammable range for that gas or vapor.

See also: Explosive Limits, Lower Explosive Limit, Lower Flammability Limit Upper Flammability Limit.

Upper Flammability Limit

The upper flammability limit is the maximum concentration by volume of a combustible substance that is capable of continued propagation of a flame under the specified conditions.

Controlling gas and vapor concentrations outside the flammable limits is a major consideration in fuel technology. The methods used to control the concentration of a potentially explosive gas or vapor include the use of sweep gas, an unreactive gas such as nitrogen to dilute the explosive gas before coming in contact with air. The use of scrubbers or adsorption resins to remove explosive gases before release is also common. Gases can also be maintained safely at concentrations above the upper explosive limit, although a breach in the storage container can lead to explosive conditions or intense fires.

Dusts also have upper and lower explosion limits. Flammability limits also depend on the particle size of the dust involved, and are not intrinsic properties of the material. In addition, a concentration above the lower explosive limit can be created suddenly from settled dust accumulations. The preferred method of managing combustible dust is by preventing accumulations of settled dust through process enclosure, ventilation, and surface cleaning.

Situations caused by evaporation of flammable liquids into the air-filled void volume of a container may be limited by flexible container volume or by using an immiscible fluid to fill the void volume.

See also: Gas Cleaning, Lower Explosive Limit, Lower Flammability Limit.

Uranium

Uranium is a chemical element (symbol U, atomic number = 92) which is a silvery-gray metal in the actinide series of the Periodic Table. A uranium atom has 92 protons and 92 electrons of which six of the electrons are valence electrons. Uranium is radioactive because all of the isotopes of uranium are unstable – the half-lives of the naturally occurring isotopes range from 159,200 years to 4.5 billion (4.5×10^9) years. The most common isotopes in natural uranium are uranium-238 (^{238}U) which has 146 neutrons and accounts for more than 99% of uranium on Earth and uranium-235 (^{235}U) which has 143 neutrons.

The many uses of uranium exploit its unique nuclear properties. For example, uranium-235 (^{235}U) is the only naturally occurring fissile isotope and is used widely in nuclear power plants and nuclear weapons. However, because of the small amounts found in nature, uranium needs to undergo enrichment so that enough uranium-235 (^{235}U) is present in the enriched product. Uranium-238 (^{238}U) is fissionable by fast neutrons and can be transmuted to fissile plutonium in a nuclear reactor. Another fissile isotope, uranium-233 (^{233}U), can be produced from natural thorium.

See also: Periodic Table of the Elements, Radioactivity, Thorium, Yellow Cake.

Urban Waste

Urban waste (municipal waste) is the waste generated by cities and municipalities and the associated landfills and is the largest source of human-related methane in the United States, accounting for 34% of these emissions. Methane is a potent greenhouse gas that contributes to smog and to the global warming of the atmosphere, remaining in the atmosphere for 9-15 years. When burned under controlled conditions rather than letting it escape into the atmosphere, methane becomes a valuable renewable energy resource that can generate electricity, heat, or fuel for vehicles.

Turning hazardous landfill gas into marketable energy adds to landfill safety, improves the environment, and decreases odors. Purified methane can be used on the premises for electricity or to fuel boilers or other thermal applications. Pipeline grade methane can be transported by pipeline for sale to the local power grid to run electric generators.

See also: Landfill, Landfill Gas, Municipal Solid Waste, Waste.

Urban Waste Briquettes

Solid waste disposal is one of the most serious urban environmental problems in developing countries. Many municipal authorities collect and adequately dispose (in places other than landfill sites) less than half of these wastes. This failure is attributed to (1) an inadequate number of landfill sites, (2) a variety of environmental regulations, (3) the absence of sufficient capacity for waste processing and recycling, and last, but not least, (4) the planned obsolescence of packaging and many of the items that form the basis of the waste.

Open or crude dumping is the most common method used by municipal authorities. Waste poses a health hazard when it lies scattered in the streets and at the dumping sites. It is now an accepted environmental philosophy that wastes have value and should be utilized based on principles of reduce, reuse, recover, and recycle. Through recycling, urban wastes can be transformed into useful products. Waste paper and leaves, in particular, provide a potentially important, alternative source of cooking fuel.

See also: Bagasse Briquettes, Briquetting, Urban Waste.

Vapor Density

The vapor density is an important property of gases and low-boiling liquids. Once gases (and low-boiling liquids) are produced under the landfill surface, they generally move away from the landfill. These products, especially the gases, tend to expand and fill the available space, so that they move or *migrate* through the limited pore spaces within the refuse and soils covering of the landfill. The tendency of some landfill gases, such as methane, that is less dense than air, is to move upward, usually through the landfill surface. However, of the hydrocarbon derivatives, methane is the only one that is less dense than air. Higher-molecular-weight hydrocarbon derivatives such as ethane, propane, and butane are denser than air (Table V-1) and may collect in pockets rather than migrate with the methane. In addition, the methane may have a pronounced solubility in the hydrocarbon liquids.

Table V-1 Density and vapor density of the lower-boiling hydrocarbon derivatives.

Hydrocarbon	Molecular weight	Specific gravity	Vapor density, air = 1
Methane	16	0.553	0.56
Ethane	30	0.572	1.04
Propane	44	0.504	1.50
Butane	58	0.601	2.11
Pentane	72	0.626	2.48
Hexane	86	0.659	3.00

The pockets of gas that do not move out of the landfill can cause safety issues when the pockets are suddenly opened to the air (for example, during landfill mining) and the flammability limit or flash point of the collected gas is reached.

Using landfill gas as the example, a major concern is the possibility of the gas accumulation inside buildings constructed on or close to a landfill site and forming pockets of gas around the building or inside the building. Protection of buildings is usually achieved using a dual barrier approach: low permeability gas membrane to resist the passage of gas, and some form of ventilation/extraction system to disperse the gas safely to the atmosphere. The requirements for particular developments will be specified by the relevant planning authorities. Gas monitoring may also be a requirement and, if so, it indicates that gas detectors must be installed at the most effective location.

In an industrial setting, the vapor density may be derived from a composition of the gas or liquid density with hydrogen rather than air.

Vapor Pressure

The *vapor pressure* is the force exerted on the walls of a closed container by the vaporized portion of a liquid. Conversely, it is the force that must be exerted on the liquid to prevent it from vaporizing further (ASTM D323). The vapor pressure increases with temperature for any given gasoline, liquefied petroleum gas, or other products. The temperature at which the vapor pressure of a liquid, either a pure compound or a mixture of many compounds, equals 1 atmosphere (14.7 psi, absolute) is designated as the boiling point of the liquid.

The vapor pressure of a chemical provides an indication of its volatility at any specific temperature. As an approximation, the vapor pressure p of a pure chemical is given by the equation:

$$\log_e p = (A/T) + B$$

A and B are empirically determined constants, and T is the absolute temperature. Hence, the vapor pressure of a chemical will increase markedly with temperature.

For a component 'a' in a mixture of vapors, its partial pressure p_a is the pressure that would be exerted by that component at the same temperature if present alone in the same volumetric concentration. So, with a mixture of two components, 'a' and 'b', the total pressure is:

$$P = p_a + p_b$$

If an inert gas is also present, its pressure is additive:

$$P = p_a + p_b + p_{\text{inert}}$$

In an 'ideal mixture', the partial pressure p_a is proportional to the mole fraction y_a of the component in the gas phase:

$$p_a = y_a P$$

This partial pressure is also related to the concentration in the liquid phase expressed as mole fraction x_a by:

$$p_a = p_a^* x_a$$

In this equation, p_a^* is the vapor pressure of component 'a' at the prevailing temperature. So, if all of the components are miscible in the liquid phase, the total pressure P of a mixture is:

$$P = p_a^* x_a + p_b^* x_b + p_c^* x_c$$

As a result: (i) the flash point of any flammable liquid will be lowered if it is contaminated with a more volatile, flammable liquid, (ii) application of heat to a flammable liquid (e.g., due to radiation or flame impingement in a fire, or because of 'hot work') can generate a flammable vapor-air mixture, (iii) an increase in temperature of a toxic liquid can create an excessive concentration of toxic vapor in air which may occur as the result of an exothermic reaction, (iv) the pressure in the vapor space of an incompletely full, sealed vessel containing liquid cannot be reduced by partially draining off liquid, (v) the pressure in an incompletely full container of liquid will increase with temperature and can, in the extreme, result in rupture due to over-pressurization unless adequate relief is provided (which may occur following an uncontrolled exothermic reaction) or, alternatively, partial ejection of the contents can occur on opening, and (vi) the composition of the vapor in equilibrium with a miscible liquid mixture at any temperature, e.g., on heating during distillation, will be enriched by the more volatile components – the composition of the liquid phase produced on partial condensation will be enriched by the less volatile components, and such *fractionation* can have implications for safety in that the flammability and relative toxicity of the mixtures can change significantly.

Vegetable Oils

Vegetable oils (Table V-2) are obtained from seed oil plants such as palm, sunflower, and soya. The predominant source of vegetable oils in many countries is rapeseed oil. Vegetable oils are a major feedstock for the oleo-chemicals industry (surfactants, dispersants, and personal care products) and are now successfully entering new markets such as diesel fuel, lubricants, polyurethane monomers, functional polymer additives, and solvents.

Table V-2 Fatty acid content of some vegetable oils (%)

Vegetable Oil	Palmitic 16:0	Stearic 18:0	Palmitoleic 16:1	Oleic 18:1	Linoleic 18:2
Tallow	29.0	24.5	-	44.5	-
Coconut oil	5.0	3.0	-	6.0	-
Olive oil	14.6	-	-	75.4	10.0
Groundnut oil	8.5	6.0	-	51.6	26.0
Cotton oil	28.6	0.9	0.1	13.0	57.2
Corn oil	6.0	2.0	-	44.0	48.0
Soybean oil	11.0	2.0	-	20.0	64.0
Hazelnut kernel	4.9	2.6	0.2	81.4	10.5
Poppy seed	12.6	4.0	0.1	22.3	60.2
Rapeseed	3.5	0.9	0.1	54.1	22.3
Safflower seed	7.3	1.9	0.1	13.5	77.0
Sunflower seed	6.4	2.9	0.1	17.7	72.8
Castor oil	-	3.0	3.0	3.0	1.2

Edible vegetable oil is generally not used as fuel, but lower-quality oil can be used for this purpose. Used vegetable oil is increasingly being processed into biodiesel, or (more rarely) cleaned of water and particulates and used as a fuel. To ensure that the fuel injectors atomize the fuel in the correct pattern for efficient combustion, vegetable oil fuel must be heated to reduce its viscosity to that of diesel, either by electric coils or heat exchangers. This is easier in warm or temperate climates.

Vegetable oil can also be used in many older diesel engines that do not use common rail or unit injection electronic diesel injection systems. Due to the design of the combustion chambers in indirect injection engines, these are the best engines for use with vegetable oil. This system allows the relatively larger oil molecules more time to burn.

Oils and fats can be hydrogenated to give a diesel substitute. The resulting product is a straight chain hydrocarbon, high in cetane, low in aromatics and sulfur, and does not contain oxygen. Hydrogenated oils, which can be blended with diesel in all proportions, have several advantages over biodiesel, including good performance at low temperatures, no storage stability problems, and no susceptibility to microbial attack.

See: Bioalcohols, Biodiesel Biofuels – Second Generation, Biofuels – Third Generation, Biogas, Transesterification.

Volatile Matter

The amount of volatile products (volatile matter content) has a major impact on the tar production levels in gasifiers. Depending on the gasifier design, the volatile matter leaves the reactor at low temperatures (updraft gasifiers) or pass through a hot incandescent oxidation zone (downdraft gasifiers) where they are thermally cracked. For biomass materials, the volatile matter content varies between 50 and 80%.

Volatile matter is gases and vapors such as hydrogen, carbon monoxide, methane, tar, other hydrocarbons, carbon dioxide, and water obtained on pyrolysis. Volatile matter is the percentage of volatile products, exclusive of moisture vapor, released during the heating of coal or coke under rigidly controlled conditions. The measured weight loss of the sample corrected for moisture establishes the amount of material (volatile matter) evolved from the coal under the conditions of the test. However, the method, being empirical, requires close adherence to detailed specifications, and since the test is essentially an assay of the sample of coal on a small scale rather than a purely chemical test, it is necessary, in order that results may be comparable between different laboratories that the conditions prescribed must be followed rigidly.

The type of heating equipment and the size and shape of the sample holders as well as the material from which they are made (platinum crucibles specified) all have some influence on the rate of heating of the sample and the range of temperatures to which it is exposed. The crucibles used are 10 to 20 ml capacity of specified size with deep-fitting lids. And there are two procedures for determination of volatile matter.

The determination of the volatile matter content of a carbonaceous feedstock is an important because volatile matter data are an integral part of evaluating some feedstocks for suitability for combustion and carbonization. The methods for determining volatile matter content are based on the same principle and consist of heating a weighed sample of the feedstock (usually approximately 1 g) in a covered crucible to a predetermined temperature; the loss in weight (excluding losses due to water) is the volatile matter content (expressed as a weight percent).

Content

The term *volatile matter content* (of coal) is actually a misnomer insofar as the majority of the volatile matter is the volatile product of the thermal decomposition of coal through the application of high temperatures. The extent to which the more volatile smaller molecules of coal add to this is dependent on the coal and should be determined by other non-destructive methods such as extraction by solvent(s). Relative yields and boiling point profiles provide the extent to which natural molecules contribute to the volatile matter without any influence from high temperature cracking.

The volatile matter obtained during the pyrolysis of coal consists mainly of combustible gases such as hydrogen, carbon monoxide, methane plus other hydrocarbons; tar as well as incombustible gases such as carbon dioxide and steam are also evolved.

The moisture that can be evolved by heating to temperatures only slightly higher than the boiling point of water is not included here, but the water formed as part of the thermal decomposition process (and that originally existed as part of the coal substance but in a form other than water) is included.

The amount of volatile matter has a major impact on the tar production levels in gasifiers. Depending on the gasifier design, the volatile matter leaves the reactor at low temperatures (updraft gasifiers) or passes through a hot incandescent oxidation zone (downdraft gasifiers) where it is thermally cracked. For biomass materials, the volatile matter content varies between 50 and 80%.

Effect of Mineral Matter

Mineral matter may also contribute to the volatile matter by virtue of the loss of water from the clays, the loss of carbon dioxide from carbonate minerals, the loss of sulfur from pyrite (FeS_2), and the generation of hydrogen chloride from chloride minerals as well as various reactions that occur within the minerals, thereby influencing the analytical data.

The characterization of coal either as agglomerating or as non-agglomerating for the purposes of rank classification is carried out in conjunction with the determination of the volatile matter content. Thus, if the residue remaining from the determination is in the form of an agglomerate button that is capable of supporting a 500-g weight without pulverization of the button or if the button shows swelling or cell structure, the coal is classified as agglomerating.

Volatile Organic Compounds

Organic compounds that evaporate easily are collectively referred to as volatile organic compounds (VOCs). Microbial volatile organic compounds (MVOCs) are a variety of compounds formed in the metabolism of fungi and bacteria (Korpi et al., 2009). Typically, a volatile organic compound is any organic compound that will evaporate at the temperature of use and which, by a photochemical reaction, will cause oxygen in the air to be converted into smog-promoting ozone under favorable climatic conditions.

Thus, volatile organic compounds are gases that are emitted into the air from products or processes (Table 6.8). Some are harmful by themselves, including some that cause cancer. In addition, they can react with other gases and form other air pollutants after they are in the air. Many volatile organic compounds have been classified as toxic and carcinogenic. They are found in a wide variety of commercial, industrial, and residential products including fuel oils, gasoline, solvents, cleaners and degreasers, paints, inks, dyes, refrigerants, and pesticides. When volatile organic compounds are spilled or improperly disposed, they can soak into the soil and eventually end up in groundwater. Volatile organic compounds (VOCs) are found in almost all natural and synthetic materials and are commonly used in fuels, fuel additives, solvents, perfumes, flavor additives, and deodorants. Potential health hazards and environmental degradation resulting from the widespread use of volatile organic compounds has prompted increasing concern among scientists, industry, and the general public (Table 6.9).

Typically, volatile organic compounds are organic chemicals that have a high vapor pressure at ordinary room temperature. The high vapor pressure results from a low boiling point, which causes large numbers of molecules to evaporate from the liquid form or sublime from the solid form of the compound and enter the surrounding air. Volatile organic compounds are numerous, varied, and ubiquitous. They include both human-made and naturally occurring chemical compounds. Many volatile organic compounds are dangerous to human health or cause harm to the environment. Anthropogenic volatile organic compounds are regulated by law, especially indoors, where concentrations are the highest. Harmful volatile organic compounds typically are not acutely toxic, but have compounding long-term health effects.

Non-methane volatile organic compounds (NMVOCs) are a collection of organic compounds that differ widely in their chemical composition but display similar behavior in the atmosphere. NMVOCs are emitted into the atmosphere from a large number of sources including combustion activities, solvent use, and production processes. NMVOCs contribute to the formation of ground-level (tropospheric) ozone. In addition, certain NMVOC species or species groups such as benzene and 1,3 butadiene are hazardous to human health. Quantifying the emissions of total NMVOCs provides an indicator of the emission trends of the most hazardous NMVOCs.

Wood smoke forms when the wood is made up of a complex mixture of gases and fine particles (particulate matter, PM). In addition to particle pollution, wood smoke contains several toxic harmful air pollutants including benzene, formaldehyde, acrolein, and polycyclic aromatic hydrocarbon derivatives (PAHs, also known as polynuclear aromatic hydrocarbon derivatives, PNAs).

Wood smoke is by far the most compelling argument against wood heating. In cold climates, a frigid, stagnant air mass traps the smoke close to the ground. In the process of wood combustion, wood vaporizes when heated into gases and tar particles. If the temperature is high enough, the tar particles vaporize into chemicals and carbon particles. If the temperature is higher still and there is oxygen present, the gases and particles burn in bright flames.

Chemically, wood is approximately 50% w/w carbon, and the rest is mostly made up of oxygen and hydrogen. When a piece of wood is heated, it starts to smoke and turn black at the same time. This is because the other products vaporize under intense heat faster than the carbon burns, so smoking leaves much of the carbon behind until only charcoal remains. The smoke that vaporizes out of the wood is a cloud of nasty, gooey little droplets of a tar-like liquid. Chemically, these droplets are actually big, gooey, complicated hydrocarbon molecules that take a number of different forms, mostly bad.

When wood is burned correctly in a bright, hot, turbulent fire, what is observed is the tar droplets rising off the wood into a zone of extreme heat where they re-vaporize, undergoing thermal decomposition into (for the most part) gaseous constituents. This leaves carbon dioxide, some carbon monoxide and a number of other gases, water vapor, and some not quite completely oxidized hydrocarbon products (typically identified as particulate emissions).

The sentiment that wood smoke, being a natural substance, must be benign to humans is still sometimes heard. It is now well established, however, that wood-burning stoves and fireplaces as well as wild fires and agricultural fires emit significant quantities of known health-damaging pollutants, including several carcinogenic compounds (Naeher et al., 2007). Two of the principal gaseous pollutants in wood smoke, carbon monoxide (CO) and the oxides of nitrogen (NO_x), add to the atmospheric levels of these regulated gases emitted by other combustion sources. Thus, there are two issues related to wood smoke and they are (i) whether or not woodsmoke should be regulated and/or managed separately, even though some of the individual constituents are already regulated in many jurisdictions and (ii) whether or not woodsmoke particles pose different levels of risk than other ambient particles of similar size.

The particulate matter wood smoke is extremely small and therefore are not filtered out by the nose or the upper respiratory system. Instead, these small particles end up deep in the lungs where they remain for months, causing structural damage and chemical changes. The carcinogenic chemicals in wood smoke adhere to these tiny particles, which enter deep into the lungs.

Volatile organic compounds (VOCs) are regulated because they are precursors to ozone: carbon-containing gases and vapors from incomplete gasoline combustion and from the evaporation of solvents.

A wide range of carbon-based molecules, such as aldehyde derivatives, ketone derivatives, and other low-boiling hydrocarbon derivatives fall within the class of volatile organic compounds. The term is often used in a legal or regulatory context, and in such cases, the precise definition is a matter of law. These definitions can be contradictory and may contain loopholes such as exceptions, exemptions, and exclusions. The United States Environmental Protection Agency (EPA) defines volatile organic compounds as any organic compound that participates in a photoreaction;

others believe this definition is broad and vague as organics that are not volatile in the sense that they vaporize under normal conditions can be considered volatile by this definition. The term may refer both to well-characterized organic compounds and to mixtures of variable composition.

See also: Wood Smoke.

Volatility, Flammability, and Explosive Properties

The boiling point (boiling temperature) of a substance is the temperature at which the vapor pressure of the substance is equal to atmospheric pressure. At the boiling point, a substance changes its state from liquid to gas. A stricter definition of boiling point is the temperature at which the liquid and vapor (gas) phases of a substance can exist in equilibrium. When heat is applied to a liquid, the temperature of the liquid rises until the *vapor pressure* of the liquid equals the pressure of the surrounding atmosphere (gases). At this point, there is no further rise in temperature, and the additional heat energy supplied is absorbed as *latent heat* of vaporization to transform the liquid into gas. This transformation occurs not only at the surface of the liquid (as in the case of *evaporation*) but also throughout the volume of the liquid, where bubbles of gas are formed. The boiling point of a liquid is lowered if the pressure of the surrounding atmosphere (gases) is decreased. On the other hand, if the pressure of the surrounding atmosphere (gases) is increased, the boiling point is raised. For this reason, it is customary when the boiling point of a substance is given to include the pressure at which it is observed, if that pressure is other than standard, i.e., 760 mm of mercury or 1 atmosphere (STP, Standard Temperature and Pressure).

The boiling points of fuels from conventional sources and from renewable energy sources are rarely, if ever, distinct temperatures and it is, in fact, more correct to refer to the boiling ranges of the various fractions. To determine these ranges, the material in question is tested in various methods of distillation, either at atmospheric pressure or at reduced pressure. Thus, the boiling points of the hydrocarbon constituents increase with molecular weight, and the initial boiling point of a (gaseous or liquid) mixture corresponds to the boiling point of the most volatile constituent.

The *flash point* of a fuel is the temperature to which the product must be heated under specified conditions to give off sufficient vapor to form a mixture with air that can be ignited momentarily by a specified flame. As with other properties, the flash point is dependent on the composition of the fuel.

The *fire point* is the temperature to which the fuel must be heated under the prescribed conditions of the method to burn continuously when the mixture of vapor and air is ignited by a specified flame. In addition to the fire point, and also from the viewpoint of safety, information related to the flash point is of most significance at or slightly above the maximum temperatures that may be encountered in storage, transportation, and use of the fuel in either closed or open containers. In this temperature range, the relative fire and explosion hazard can be estimated from the flash point. For products with flash point below 40°C (104°F), special precautions are necessary for safe handling. Flash points above 60°C (140°F) gradually lose their safety significance until they become indirect measures of some other quality.

A further aspect of volatility that receives considerable attention is the vapor pressure of the fuel. The *vapor pressure* is the force exerted on the walls of a closed container by the vaporized portion of a liquid. Conversely, it is the force that must be exerted on the liquid to prevent it from vaporizing further. The temperature at which the vapor pressure of a liquid fuel (which may be a pure compound or a mixture of many compounds) equals 1 atmosphere (14.7 psi, absolute) and is designated as the boiling point of the liquid.

The flammable range is expressed by the lower explosive limit (LEL) and the upper explosive limit (UEL). The lower explosive limit is the concentration of the fuel in the air below which the propagation of a flame will not occur on contact with an ignition source. The upper explosive limit is the concentration of the fuel in the air above which the propagation of a flame will not occur on contact with an ignition source.

See also: Lower Explosive Limit, Lower Flammability Limit, Upper Explosive Limit, Lower Flammability Limit.

Walker Circulation

In a manner similar to the Hadley Cell that transports air from the equator to the sub-tropical latitudes (meridional circulation), there are zonal mean circulations (east-west oriented). One of these, the Walker circulation, plays a primary role in determining where rainfall will fall near equatorial regions and throughout the globe. Under normal conditions, the easterly trade winds move warm surface waters westward, causing higher temperatures in the western Pacific. The air overlying this warm water is in turn heated and rises to high levels of the atmosphere, diverges outwards, east and west, and finally sinks over the eastern Pacific. Rising air is associated with a region of low pressure, towering cumulonimbus clouds, and rain. High pressure and dry conditions accompany the sinking air. There is also upwelling of cold nutrient-rich water off the coast of Peru.

However, in contrast to the Hadley, Ferrel, and polar circulations that run along north-south lines, the Walker circulation is an east-west circulation. Over the eastern Pacific Ocean, surface high pressure off the west coast of South America enhances the strength of the easterly trade winds found near the equator. The winds blow away from the high pressure toward lower pressure near Indonesia. Upwelling, the rising of colder water from the deep ocean to the surface, occurs in the eastern Pacific along South America near Ecuador and Peru.

This cold water is especially nutrient-rich and is stocked with an abundance of large fish populations. By contrast, the water in the western Pacific, near Indonesia, is relatively warm. The air over Indonesia rises because of the surface low pressure located there and forms clouds. This causes heavy precipitation to fall over the western tropical Pacific throughout the year. The air then circulates back aloft toward the region above the surface high pressure near Ecuador, and this becomes the Walker circulation. The air sinks at this surface high pressure and is picked up by the strong trade winds to continue the cycle.

On some occasions, the Walker circulation and the trade winds weaken, allowing warmer water to move toward the eastern tropical Pacific near South America. This warming of the eastern Pacific Ocean (El Niño) allows the warmer water to also serve as a source for warm, moist air which can aid in the development of heavy thunderstorms over the mass of warm water.

See also: Coriolis Force, Ferrel Cell, Hadley Cell, Polar Cell, Wind Energy, Wind Power.

Waste

Waste is the remains or by-product from a process for which no use is planned or foreseen. The words domestic (or municipal) and industrial are qualifiers of the source of the waste and, to some extent, also descriptive of the contents of the waste. Once a material has been designated as waste, it remains waste until it has been fully recovered and no longer poses a potential threat to the environment.

Thus, domestic waste (also known as rubbish, garbage, trash, or junk) is unwanted or undesired material (although the old adage one man's waste is another man's treasure sometimes applies). Waste is the general term; though the other terms are used loosely as synonyms, they have more specific meanings: rubbish or trash are mixed household waste including paper and packaging; food waste or garbage (North America) is kitchen and table waste, and junk or scrap is metallic or industrial material. There are other categories of waste as well: sewage, ash, manure, and plant materials from garden operations, including grass cuttings, fallen leaves, and pruned branches.

On the other hand, industrial waste is waste type produced by industrial factories, mills, and mines. It has existed since the outset of the industrial revolution. Toxic waste and chemical waste are two more specific designations of industrial waste.

Municipal solid waste (MSW) is a waste type (Table W-1) that originates from various sources (Table W-2) and includes predominantly household waste (domestic waste) with sometimes the addition of commercial wastes

collected by a municipality within a given area. They are in either solid or semisolid form and generally exclude industrial hazardous waste. The term residual waste relates to waste left from household sources containing materials that have not been separated out or sent for reprocessing.

Table W-1 Types of waste.

Type	Description
Food waste	Animal, fruit, or vegetable residues (also called garbage) that result from the handling, preparation, cooking, and eating of foods. Also, food wastes are subject to putrefaction insofar as they will decompose rapidly, especially in warm weather.
Garbage (rubbish)	Combustible and non-combustible solid wastes, excluding food wastes or materials subject to putrefaction. Typically combustible rubbish consists of materials such as paper, cardboard, plastics, textiles, rubber, leather, wood, furniture, and garden (landscaping) trimmings. Non-combustible garbage rubbish consists of items such as glass, crockery, tin cans, aluminum cans, ferrous and non-ferrous metals, dirt, and construction material.
Ash	Materials ranging from the burning of wood, coal, coke, and other residues of combustible wastes. Ash and residues are typically composed of fine powder, cinders, clinkers, and small amounts of burned and partially burned materials.
Demolition/construction	Wastes from razed buildings and other structures are classified as construction demolition wastes as are wastes from the construction, remodeling, and repairing of residential, commercial, and industrial buildings and similar structures are classified. These wastes may include dirt stones, concrete, bricks, plaster, lumber, shingles (tiles) as well as plumbing, heating waste, and electrical parts. These waste are usually of an inert nature. The main exception is asbestos for which special disposal is required.
Treatment plant waste	The solid and semi-solid wastes from water, sewage, and industrial wastewater treatment facilities are included in this classification. Sewage sludge is a slurry of fine organic-rich particles with a highly variable chemical composition depending on the source of the effluent as well as the types and efficiency of the treatment process. Sewage sludge tends to concentrate heavy metals and water-soluble synthetic organic compounds but may also contain grease, oil, and bacteria. Dredged materials are those materials that are excavated from river estuaries, harbors, and other waterways to aid navigation. Much of the dredged material may be contaminated crude oil, crude oil products, heavy metals, nutrients, and organo-chlorine compounds.
Other (special) waste	Wastes such as street sweepings, roadside litter, catch-basin debris, dead animals, abandoned vehicles, and electrical appliances fall into the class of special waste.

Table W-2 Sources of municipal waste.

Source	Types
Residential	Food waste Garbage Ash Hazardous waste
Commercial	Food waste Garbage Ash Demolition waste Construction waste Treatment plane sludge Hazardous waste

There are five broad categories of municipal solid waste which are (i) biodegradable waste such as food and kitchen waste, green waste, and paper – which can also be recycled, (ii) recyclable material such as paper, glass, bottles, cans, metals, and certain plastics, (iii) inert waste such as construction and demolition waste, dirt, rocks, and debris, (iv) composite waste which includes waste clothing and waste plastics such as toys, and (v) domestic hazardous waste (also called household hazardous waste) and toxic waste such as discarded medications, paint, chemicals, light bulbs, fluorescent tubes, spray cans, fertilizer containers, pesticide containers, batteries, and shoe polish.

There is also electronic waste which is a waste consisting of any broken or unwanted electrical or electronic appliance. While there is no generally accepted definition of electronic waste, in most cases, electronic waste consists of electronic products that were used for data processing, telecommunications, or entertainment in private households and businesses that are now considered obsolete, broken, irreparable, or of no further use due to planned obsolescence. Despite its common classification as a waste, disposed electronics are a considerable category of secondary resource due to their significant suitability for direct reuse (for example, many fully functional computers and components are discarded during upgrades), refurbishing, and material recycling of its constituents.

It is a point of concern considering that many components of such equipment are considered toxic and are not biodegradable but they are not precursors to fuels and, other than recognition though the above paragraph, will not be considered in the context of the present text.

In nature, there is no waste; on the other hand, waste is a by-product of the human economic system and the technology that drives it. Since the industrial revolution, human society has developed economies that are largely unrelated from nature and the natural order of events. They have created public and private wealth, material well-being, a plentiful food supply, comfortable living conditions, personal freedoms, and enhanced culture, but at a price.

In modern society, waste comes in a variety of forms and must be dealt with on a day-to-day basis. Industry produces huge amounts of industrial waste, and domestic waste makes a large contribution to the general waste problem. In spite of the recognition, many insidious waste products escape (inadvertently or deliberately) into the surrounding environment. Thus, there are numerous pollution incidents. On the other hand, there are technologies available for the treatment of most of the wastes produced. The level of treatment is largely a matter of cost, but conversion of waste to new products is a concept that has long been ready to hatch. Now is the time.

See also: Anaerobic Digestion, Digesters, Municipal Solid Waste, Urban

Waste Biomass

Biomass is the material derived from plants that use sunlight to grow which includes plant and animal material such as wood from forests, material left over from agricultural and forestry processes, and organic industrial, human, and animal wastes. More simply, biomass is stored energy. During photosynthesis, plants use light from the Sun's energy (light energy) to convert carbon dioxide and water into simple sugars and oxygen.

In nature, if biomass is left undisturbed on the ground, it will break down over a long period of time, releasing carbon dioxide and its store of energy slowly. By burning biomass, its store of energy is released quickly and often in a useful way. So converting biomass into useful energy imitates the natural processes but at a faster rate.

Biomass wastes can be transformed into clean energy and/or fuels by a variety of technologies, ranging from conventional combustion process to state-of-the-art thermal depolymerization technology. Besides recovery of substantial energy, these technologies can lead to a substantial reduction in the overall waste quantities requiring final disposal, which can be better managed for safe disposal in a controlled manner while meeting the pollution control standards.

Biomass wastes can be transformed into clean energy and/or fuels by a variety of technologies, ranging from conventional combustion process to state-of-the-art thermal depolymerization technology. Besides recovery of substantial energy, these technologies can lead to a substantial reduction in the overall waste quantities requiring final disposal, which can be better managed for safe disposal in a controlled manner while meeting the pollution control standards.

See also: Biomass Waste.

Waste – Domestic and Industrial

Industrial waste is waste type produced by industrial factories, mills, and mines. It has existed since the outset of the industrial revolution. Toxic waste and chemical waste are two designations of industrial waste.

Domestic waste is waste from householders which cannot be recycled, composted, reused, or disposed of by other means.

Much of what human society discards contains usable material, much of it in the form of recoverable energy. Paper, wood, cloth, food waste, and plastics are the main potential energy sources in waste. The remainder of the waste consists of glass, metals, and miscellaneous rubble. Domestic waste is typically disposed of by tipping it into large holes in the ground – landfill sites. Sometimes, the waste is incinerated first, and only the remaining ash and non-combustible material is sent to a landfill. Increasingly, a proportion of the waste is being separated for recycling at some stage along the way.

It is possible to recover energy from landfill sites and from waste incinerators. Domestic waste could also provide feedstock for a number of other conversion systems, all of which could recover useful energy while reducing the requirement for landfill sites. However, whatever the energy technology, domestic waste is a low-grade fuel. Its consistency is variable and not well suited to mechanical handling systems; the proportions of the various constituents will vary from load to load; the moisture content and heating value will vary; and the proportion of non-combustible material will keep the heating value low. All of this can lead to inefficient combustion if the process is not well controlled, making it more difficult to control toxic emissions from plastics and other materials.

There is also a potential conflict between the recycling of materials and the recovery of energy from those materials. The main benefit of domestic waste as a fuel source is that, as with most other waste streams, energy technology can reduce the waste disposal problem.

Recently, interest has grown in the burning of garbage/domestic waste to produce electricity. This is not a new idea, although in the past, when waste was burned, it created pollution that could even be toxic. Today, the technology exists to remove almost all the pollutants from the fumes produced during the energy production cycle. Special filters remove dangerous chemicals and particles that would normally be found in the fumes. The domestic waste is sorted usually by hand to remove materials than can be recycled. Steel is removed using electromagnets, and this is stored until there is enough quantity for recycling to be economically viable. Aluminum, in the form of cans is removed by hand. The waste is then fed into the hopper of a furnace. When the doors slide open, it falls into the burning chamber. Gas is normally used to start the fire which burns at a high temperature, destroying the domestic waste. While the waste burns, it heats a water tank, in turn, producing steam. The steam is used to turn turbines, producing electricity. Once steam has been produced, the production of electrical power is no different than that used in any other power station. The high-pressure steam is used to turn electrical turbines which produce electricity. The advantage of this way of producing electricity is that the domestic waste that would normally be buried in landfill sites or even dumped far out at sea is burned. This means that vast areas of land that would have to be used for landfill are free for agriculture or for building.

See also: Municipal Solid Waste, Urban Waste.

Waste – Effects of

Wastes generated from the domestic and industrial sources increase continuously with rising population. In general, the lack of facilities for disposal of waste caused overall of landfill sites resulting in hazards for the environment and for public health. These effects include the following: (i) air pollution, (ii) pollution of surface waters, (iii) changes in soil fertility, and (iv) changes in the landscape and visual discomfort.

Air pollution by unpleasant odors and wind-carried suspensions is obvious in areas located nearby urban waste landfills, since these are currently run in complete ignorance of practices such as cell operation and inert matter lagging. The leakage on the slopes of landfills situated nearby surface water bodies adds to the pollution of such waters by organic substances and suspensions. The urban waste landfills that are not waterproof often represent sources of

groundwater pollution by nitrates and nitrites, as well as other pollutants. Water leakage adversely affects the quality of the adjoining soils, which brings along consequential effects to their utilization.

Withdrawing land from the natural or economic circuit in order to set up waste landfills is a process which may be regarded as temporary, yet, in terms of sustainable development, it extends over at least two generations when adding up the time periods required for planning works (1 to 3 years), running (15 to 30 years), ecological reconstruction, and subsequent monitoring (15 to 20 years).

In terms of biodiversity, any domestic or industrial waste landfill means the subsequent elimination of a number of 30 to 300 species (microbiological population of the soil not included) on each hectare of the area intended to host a landfill. Moreover, changes are likely to occur in areas close to the landfill, such as (i) ruderal species, i.e., plant species that are first to colonize disturbed lands that are specific to polluted areas would become dominant in the vegetal assemblies, and (ii) some mammals, birds, and insects would desert the area, in favor of species that feed on refuse (rats, crows).

Although the effects on flora and fauna are, in theory, time limited to the period over which the landfill is operated, the ecological reconstruction performed after the area has been relieved from its technological use will not be able to retrieve the initial biological balance, as the evolution of that biosystem has been irreversibly modified. The practices used currently in the collection, transport, and storage of urban waste facilitate the multiplication and dissemination of the pathogenic agents and their accompanying breed: insects, rats, crows, and stray dogs.

Thus, waste in any form (domestic or industrial) represents a health hazard, due to its dispersal and composition. In terms of composition, the focus is often on toxic substances such as heavy metals (lead, cadmium), pesticides, solvents, and used oils that form an integral part of the waste.

Indeed, the challenge for waste disposal arises from the joint storage of hazardous materials (including toxic sludge, oil products, dyeing residues, and metallurgical slag) and solid domestic waste. This situation is likely to generate inflammable, explosive, or corrosive mixtures and combinations thereof. On the other hand, the presence of easily degradable household may facilitate the decomposition of complex hazardous components, and thus diminish environmental pollution.

Another negative aspect is the fact that several recyclable and useful materials are stored in the same place as materials that cannot be recycled; consequently, these materials blend together and become chemically and biologically contaminated, which renders their retrieval rather difficult.

Thus, the problems faced by waste management activities may be summarized as follows: (i) storage in open grounds is the most used method to remove waste ultimately, (ii) existing landfills may be located in sensitive places (i.e., in the close proximity to lodgings, surface or ground water, leisure areas), (iii) existing waste landfills may be improperly designed from an environmental protection point of view, thus allowing for water and soil pollution in those areas, and (iv) currently, waste landfills may require a review of waste handling practices insofar as waste layers are not compacted and there is no strict control of the quality and quantity of waste that is dumped on the landfill leading to the potential for fire and/or the emanation of unpleasant odors.

All of the above lead to the conclusion that specific measures need to be taken with regard to waste management, which would be adequate in each phase of the waste dumping process. Environmental monitoring activities should comprise the observance of these measures. However, one answer to these issues is to convert the waste to usable products either through (i) the production of gaseous fuels, or (ii) the production of liquid fuels, or (iii) the production of solid fuels.

Such efforts may not only solve the depletion of fuels from fossil sources but also assist in the disposal of waste materials and the ensuing environmental issues. However, before entering upon the process descriptions for waste conversion, it is necessary to understand the composition of domestic and industrial waste.

The term waste incorporates a number of streams in a modern society. Relevant to gasification, pyrolysis, and incineration are streams such as chemical waste, medical waste, waste from auto-shredder, paper, plastics, textiles, metals, glass, and sundry other components which may form part of the industrial waste and domestic waste. Like feedstocks for any process, these raw materials require different processes for optimal operation.

Generating waste at current levels is incompatible with a sustainable future. While the problem of waste is serious, a variety of initiatives are being taken to address the various threats. These include moves toward waste minimization, waste segregation, and recycling, cleaner production with regular waste audits, green chemistry, renewable

energy and energy efficiency, and developing the concept of industrial ecosystems. The issues involved are much more than technical problem.

The historic approach to solid waste has been to bury it in landfill. This is becoming increasingly problematic because the diminishing availability of suitable landfill sites and the increasingly stringent conditions being applied to landfill mean that charges have increased and will continue to increase. Major problems associated with landfills are the leachate containing toxic heavy metals and the methane gas that is produced.

This is a major issue because of the variability of industrial solid, liquid, and gaseous wastes, and the capacity of modern processing industries to produce huge quantities of waste. Fortunately, regulatory processes are now such that the numerous disasters caused previously should not be repeated. However there are remaining problem sites that constitute long-term hazards.

Thus, in order to reduce the amount of landfill, the amount of waste must be reduced. This involves either (i) cutting back on the use of many materials or (ii) use of the waste by conversion to useful products. Either option would reduce the amount of waste sent to landfill sites. The first option certainly reduces the amount of landfill material but is often more difficult to achieve. However, the second option offers the attractive proposition of the production of fuel products. Thus, waste conversion becomes an attractive option to landfill disposal, and the result is the generation of a usable product in the form of a gaseous, liquid, or solid fuel.

However, ancillary of the second option is the heterogeneity of waste material. In fact, it is obvious that many waste streams are not subject to direct processing and will require special measures in the form of specific pretreatment of the waste prior to processing.

One form of pretreatment is separation and recycling of waste components, thereby removing a portion of the waste stream for recycling and other uses. The result of this separation at the source is the remaining residual waste (i.e., the waste stream from which recyclable materials have been removed) that is not destined for any use other than landfill is sent to the conversion reactor.

See also: Municipal Solid Waste, Urban Waste, Waste – Domestic And Industrial.

Waste – Fuels From

A significant number and variety of organic wastes are combusted in energy recovery systems including municipal solid waste, various forms of refuse-derived fuel produced from municipal solid waste as well as a broad range of other specific specialty wastes. The practice of incinerating waste has become increasingly prevalent in order to accomplish disposal in an environmentally sensitive manner. Combustion of such wastes reduces the volume of material which must be sent to a landfill, reduces the airborne emissions resulting from plant operations and landfill operations, and permits some economic benefit through energy recovery.

The technologies used to combust wastes depend on the form and location of components to be burned. The issues associated with energy generation from waste include fuel composition characteristics, combustion characteristics, formation and control of airborne emissions including both criteria pollutants and air contaminants (such as trace metals), and the characteristics of bottom and fly ash that is generated from waste combustion.

The concept of the incineration of domestic and industrial waste to gaseous fuels is one of the first suggestions from the disposal of waste and the generation of energy. With this in mind, waste incineration has been, and continues to be, practiced in many parts of the world. In fact, co-combustion of waste in (large and efficient) coal-fired power plants is an especially attractive option because of the high conversion efficiency of these plants. However, there are issues that need attention, and while it is not intended here to use the following comments to be a critique of waste incineration, here are lessons to be learned and changes to be made in this manner of waste removal.

Although not in keeping with the main context of this text, i.e., the production of fuels, the incineration of wastes is worthy of mention insofar as waste combustion (although the main goal of incineration is volume reduction with the sterilization of the waste as a significant side-effect) can be a source of energy but, generally. Thus, the incineration process may also be used to produce steam and electricity. However, as the moisture content of the waste increases, a self-sustaining combustion process is not possible. Nevertheless, domestic waste and industrial waste are feedstocks for incinerators.

Nevertheless, incineration is recognized as a waste treatment technology for disposal of the organic constituents of the waste. Incineration and other high-temperature waste treatment systems convert the waste into ash, flue gases, particulate matter, and heat, which can in turn be used to generate electricity. The flue gases are cleaned for pollutants before it is dispersed in the atmosphere. Furthermore, incineration with energy recovery is one of several waste-to-energy technologies which include gasification and anaerobic digestion.

Modern incinerators reduce the volume of the original waste by 95 to 96%, depending upon composition and degree of recovery of materials such as metals from the ash for recycling. While incineration does not replace land-filling, it does reduce the necessary volume significantly. In fact, incineration has particularly strong benefits for the treatment of certain types of waste in niche areas such as clinical waste and certain hazardous waste where pathogens and toxins can be destroyed by high temperatures.

The incinerator is, simply, a furnace for burning refuse, and modern incinerators include pollution mitigation equipment such as flue-gas cleaning. The incinerator must be designed to ensure that the flue gas reaches a temperature of at least 850°C (1,560°F) in order to ensure proper breakdown of organic toxins. This includes backup auxiliary burners (often fueled by oil), which are fired into the boiler in case the heating value of the waste becomes too low to reach this temperature alone. The flue gas is then cooled by heat transfer and heat the steam to typically 400°C (750°F) at a pressure of 550 to 600 psi for the electricity generation in the turbine. At this point, the flue gas has a temperature of around 200°C (390°F), and is passed to the flue gas cleaning system. There are various types of incinerator plant design: (i) simple incinerator, (ii) fixed or moving grate incinerator, (iii) rotary-kiln incinerator, and (iv) the fluidized bed incinerator.

The *simple incinerator* is an older and simpler kind of incinerator that is, essentially, a brick-lined cell with a metal grate over a lower ash pit, with one opening in the top or side for loading and another opening in the side for removing incombustible solids (clinker). Many small incinerators formerly found in apartment houses have now been replaced by waste compactors. The *fixed* or *moving grate incinerator* is a fixed hearth incinerator with a moving grate. The moving grate enables the movement of waste through the combustion chamber to be optimized to allow a more efficient and complete combustion. These incinerators are typically used for combustion of municipal waste, and are thus referred to as municipal solid waste incinerators (MSWIs).

In the *fixed* or *moving grate incinerator*, the waste is introduced by a waste crane through the “throat” at one end of the grate, from where it moves down over the descending grate to the ash pit in the other end. Here the ash is removed through a water lock. Part of the combustion air (primary combustion air) is supplied through the grate from below. This air flow also has the purpose of cooling the grate itself. Cooling is important for the mechanical strength of the grate, and many moving grates are also water cooled internally. Secondary combustion air is supplied into the boiler at high speed through nozzles over the grate. It facilitates complete combustion of the flue gases by introducing turbulence for better mixing and by ensuring a surplus of oxygen.

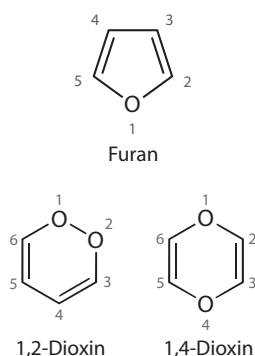
The rotary kiln incinerator has a primary chamber and secondary chamber. The primary chamber consists of an inclined refractory lined cylindrical tube. Movement of the cylinder on its axis facilitates movement of waste. In the primary chamber, there is conversion of solid fraction to gases, through volatilization, destructive distillation, and partial combustion reactions. The secondary chamber is necessary to complete gas phase combustion reactions. The clinker spills out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases may be combusted in an *afterburner*. To control air pollution, the combustion product gases are further treated with acid gas scrubbers to mitigate sulfuric acid and nitric acid emissions, and then routed through bag houses to remove particulate matter before the gases are released into the atmosphere.

The *fluidized bed incinerator* uses a strong airflow through a sand bed until a point is reached where the sand particles separate to let the air through and mixing and churning occurs, thus a fluidized bed is created and fuel and waste can now be introduced. The sand with the pre-treated waste and/or fuel is kept suspended on pumped air currents and takes on a fluid-like character. The bed is thereby thoroughly mixed and agitated keeping small inert particles and air in a fluid-like state. This allows all of the mass of waste, fuel, and sand to be fully circulated through the furnace.

The heat produced by an incinerator can be used to generate steam which may then be used to drive a turbine in order to produce electricity. However, the amount of energy produced is very much dependent upon the type and composition of the waste used as the feedstock. Much of the current thinking involves co-incineration of a specified

amount of the waste (calculated on the basis of the carbon content of the waste) with, for example, coal to produce a consistent amount of energy.

Incineration has a number of outputs such as the ash and the emission to the atmosphere of flue gas. Before the flue gas cleaning, the flue gases may contain significant amounts of particulate matter, heavy metals, dioxin derivatives, furan derivatives, sulfur dioxide, hydrochloric acid, and polynuclear aromatic hydrocarbon derivatives (carcinogens). The most publicized concerns related to the incineration of municipal solid wastes involve the fear that it produces significant emissions of furan derivatives and dioxin derivatives, which are considered to be serious health hazards.



Older generation incinerators that were not equipped with modern gas cleaning technologies were indeed significant sources of dioxin emissions. However, modern incinerators (due to advances in emission control designs and stringent regulations) must limit and even mitigate such emissions.

Particulate matter is collected by particle filtration, most often electrostatic precipitators and/or baghouse filters. Hydrogen chloride and sulfur dioxide are removed in scrubbers or by dry desulfurization in which a limestone slurry ($\text{CaCO}_3/\text{H}_2\text{O}$) is injected into the flue gas before the particle filtration. Wastewater from scrubbers must subsequently pass through a wastewater treatment plant. Nitrogen oxide (NO_x) emissions are either reduced by catalytic reduction with ammonia in a catalytic converter (selective catalytic reduction) or by a high temperature reaction with ammonia in the furnace (selective non-catalytic reduction). Heavy metals are often adsorbed on injected activated carbon powder, which is collected by the particle filtration.

Incineration produces fly ash and bottom ash just as is the case when coal is combusted. The total amount of ash produced by municipal solid waste incineration ranges from 15 to 20% w/w of the waste, and the fly ash amounts to 0 to 10% w/w of the total ash. The fly ash, by far, constitutes more of a potential health hazard than does the bottom ash because the fly ash often contains high concentrations of heavy metals such as lead, cadmium, copper, and zinc as well as small amounts of dioxin derivatives and furan derivatives. The bottom ash seldom contains significant levels of heavy metals.

While fly ash is always regarded as hazardous waste, bottom ash is generally considered safe for regular landfill after a certain level of testing defined by the local legislation. Ash, which is considered hazardous, may generally only be disposed of in landfills which are carefully designed to prevent pollutants in the ash from leaching into underground aquifers – or after chemical treatment to reduce its leaching characteristics.

In spite of the promise shown by the use of incinerators for waste disposal and, in some cases, energy production (in the form of fuel gases), the use of incinerators for waste management is controversial. On the one hand, concerns over the health effects of dioxin and furan emissions have been significantly lessened by advances in emission control designs and very stringent new governmental regulations that have resulted in large reductions in the amount of dioxins and furans emissions. Also, modern incineration plants generate electricity and heat that can be sold to the regional electric grid and can sell steam to district heating systems or industrial customers. The bottom ash residue remaining after combustion has been shown to be a non-hazardous solid waste that can be safely landfilled or possibly reused. In densely populated areas, finding space for additional landfills is becoming increasingly difficult.

Incineration of municipal solid waste avoids the release of carbon dioxide and methane. Every ton of municipal solid waste incinerated prevents approximately one ton of carbon dioxide equivalents from being released to the atmosphere. Incineration of medical waste and sewage sludge produces an end product ash that is sterile and

non-hazardous. On the other hand, the end product ash must still be safely disposed. Many countries deny the use of incineration as an option for the treatment of their municipal solid wastes because of the potential of environmental pollution.

Incinerators emit varying levels of heavy metals such as vanadium, manganese, chromium, nickel, arsenic, mercury, lead, and cadmium which can be toxic at very minute levels. Other advanced alternative technologies are available such as biological treatment combined with anaerobic digestion and gasification. Incinerators produce soot particles ($PM_{2.5}$, nanoparticles or particles with a size less than 2.5 microns, i.e., $<1 \times 10^{-6}$ meter) in the furnace. Even with modern particle filtering of the flue gases (e.g., baghouse filters), some of these small particles are emitted to the atmosphere.

Although waste combustion can be used to generate power, a portion of that power is consumed by fans, pumps, and other electrically powered components. However, with the ban on landfilling untreated waste in various countries, modern design waste-to-energy plants have been built in the last decade, with more under construction, and there is renewed interest in waste-to-energy.

In summary, incineration is not a complete method of disposal; its main advantage is that it produces a residue that is substantially reduced in volume and may be relatively inert. In addition, the efficiency of an incinerator is, on occasion, due to excessive throughput or choice of operating parameters that are less than desired. For example, the operating temperature inside the plant should be at the specified temperature (usually approximately 850°C, 1,560°F) to reduce the possible effects of the most dangerous air pollutants and the production of dioxins. A lower than specified combustion temperature implies incomplete incineration, leaving part of the waste in the ashes and other combustion residues. Furthermore, the exhaust gases may be unnecessarily polluting because of the low combustion temperature, and the by-products of such combustion may be sent to an unprotected landfill for disposal.

Gaseous Fuels

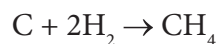
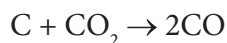
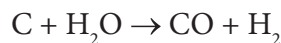
There are two ways of producing gaseous fuel from waste: (i) gasification of the waste at high temperatures by partial oxidation and then conversion of materials containing carbon into synthesis gas (mainly hydrogen and carbon monoxide) and (ii) production of biogas, mainly methane, by the anaerobic digestion of waste.

Gasification is the general term used for processes where heat is used to transform a feedstock, usually a solid feedstock such as coal or biomass or wood into a gaseous fuel. Similarly, the gasification process is also applicable to the conversion of any solid carbonaceous waste to a clean-burning gaseous fuel. Whether starting with coffee grounds, municipal trash, or junk tires, the end product is a flexible gaseous fuel, and with the relevant process modifications, production of liquid and solid fuels is also possible. Biochemical conversion options can be divided into digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol). With respect to thermochemical conversion options, a distinction can be made between combustion, gasification, and pyrolysis.

Anaerobic digestion is a process whereby organic waste is broken down in a controlled, oxygen-free environment by bacteria naturally occurring in the waste material. Methane-rich biogas is produced, thus facilitating renewable energy generation. As a result, materials that are currently going to landfill can be utilized; natural methane emissions are reduced, and conventional generation with its associated carbon emissions is displaced. The residual nutrient-rich liquor and digestate are suitable for use as fertilizer on the farmland surrounding such a plant, reducing the need for artificial fertilizer. In summary, anaerobic digestion is a form of composting and its use for the conversion of waste to gaseous fuel by anaerobic processes.

The concept of the production of fuel gas by gasification of waste is not new – solid wastes were somewhat in focus for the gasification and pyrolysis activities; around 1970, biomass gasification took over the central role when the oil prices went up after 1973 which is reflected in the development of a wide range of processes. Most of the processes were designed for wood or wood waste, and, surprisingly, some of these processes have also been proposed for waste handling and are taking up the move to commercialization that was last evident two decades ago.

The chemical principle behind waste gasification and the production of gaseous fuels is that waste contains carbon and it is this carbon that is converted to gaseous products via the usual gasification chemistry. Thus, when fuel is fed to a gasifier, water and volatile matter are released fast and a char residue is left to react further. The char gasification is what mainly controls the conversion achieved in the process. From solid carbon, product gas is formed according to the following main reactions:



In addition to the reactions of solid carbon, the most important reaction is the water-gas shift reaction, which takes place in the gas phase:



The product gas generally contains large amounts of hydrogen and carbon monoxide and a small amount of methane, as well as carbon dioxide and steam, and in air gasification nitrogen. In addition, a significant amount of other organic components in the gas, known as tar, is formed. Tar formation is a well-known phenomenon in the thermal reactions of coal and can also be anticipated to form in the gasification or pyrolysis of any complex carbonaceous material.

Biomass-based fuels (and many components of domestic and industrial waste can be included in this category) are non-fossil fuels. Vegetative biomass can be classified into the categories woody, herbaceous, agricultural by-products, energy crops, and black liquor (a by-product of the forest industry). Because of the high concentration of organic materials in industrial waste and in domestic waste (including discarded food), many constituents of waste are actually biomass. But the issues arise from the other constituents of the waste that make the waste truly heterogeneous and, in many cases, of indeterminate composition.

Most of the reactors were of the fixed-bed type (updraft or downdraft) and are considered to be adequate processes for local use in terms of the alternate, i.e., landfilling the waste. However, whether wastes should be handled locally or in large scale, centralized units are another issue that is still under debate.

Thus, a process for waste gasification must be chosen to reflect the character of the waste relation to the main questions in this report as stated in the introduction. However, a few of the original processes touted as potential methods for waste gasification may not be in current commercial use and reference must be made to gasification processes (for coal) that are in current commercial use.

The reason for the overall lack of commercial processes for waste gasification hinges on several areas. For example, most of the processes proposed for waste gasification did not include a separation step. Feedstock homogeneity is a pre-requisite for many gasifiers, and feedstock heterogeneity and process scale-up can lead to a number of mechanical problems, shut-downs, sintering, and hot spots leading to corrosion and eventual failure of the reactor wall.

In addition, most of these process efforts included use of a fixed bed reactor on the basis of applicability of coal gasification is also applicable to waste. The most common equipment was a shaft reactor with a bottom temperature of approximately 1,000°C (1,830°F) leading to transport problems within the reactor bed and in the shaft to the ash outlet, such as ash sintering. The character of coal ash and its effect on gasification are well understood. The effect of ash from waste is not yet fully understood and requires extra effort before a suitable reactor can be proposed for waste gasification.

Finally, most of the systems proposed for waste gasification produced tar or a mixture of tar and gas and very few of the processes included gas cleaning. Thus, the tar-rich gas caused problems on the gas side as well as tar condensation in the pipes to the combustor. On the other hand, waste that contained metals, glass, and inorganic materials which sinter and melt at higher temperatures also caused reactor problems.

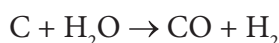
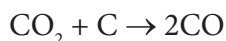
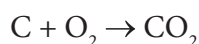
Overall, the heterogeneous composition of domestic and industrial waste has not been beneficial in terms of the gasification of the waste. Recycling programs in which the first is first separated into various components may be a necessary prelude to waste gasification. With energy prices (crude oil and natural gas) currently at an all-time high, and threatening to continue at high levels for the foreseeable future, the time is now for the development of waste gasification processes.

Liquid Fuels

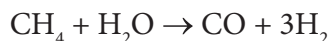
Using ethanol as the example, numerous waste streams could be exploited for ethanol production. Some waste streams currently under consideration include mixed paper from municipal solid waste, cellulosic fiber fines from recycled paper mills, as well as various bio-feedstocks. However, each waste stream has its own unique characteristics, and they generally vary from one source or time to another. Therefore, ethanol or, for that matter, the production of liquid fuels from waste streams is not only feedstock dependent but is also process dependent.

Using the term loosely, the standard way of preparing liquid fuels from carbonaceous material is (i) to gasify the feedstock to produce synthesis gas and then (ii) convert the synthesis gas by the Fischer-Tropsch reaction to hydrocarbon derivatives. Briefly, synthesis gas (syngas) is the name given to a gas mixture that contains varying amounts of carbon monoxide and hydrogen generated by the gasification of a carbonaceous fuel to a gaseous product with a heating value. Examples include steam reforming of natural gas or liquid hydrocarbon derivatives to produce hydrogen, the gasification of coal, and in some types of waste-to-energy gasification facilities.

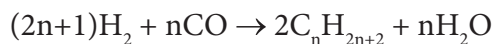
Synthesis gas consists primarily of carbon monoxide and hydrogen, with small amounts of carbon dioxide present in the raw (unpurified) gas carbon dioxide, and hydrogen and has less than half the energy density of natural gas. Synthesis gas is combustible and often used as a fuel source or as an intermediate for the production of other chemicals. Synthesis gas for use as a fuel is most often produced by gasification of coal or municipal waste mainly by the following paths:



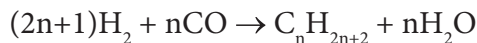
When used as an intermediate in the large scale, industrial synthesis of hydrogen and ammonia, it is also produced from natural gas (via the steam reforming reaction) as follows:



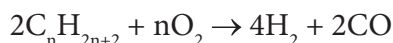
The Fischer-Tropsch synthesis is, in principle, a carbon chain building process, where methylene groups are attached to the carbon chain. The actual reactions that occur have been, and remain, a matter of controversy, as it has been in the last century since 1930s.



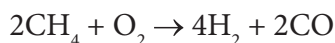
Even though the overall Fischer-Tropsch process is described by the following simple chemical equation:



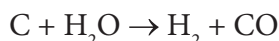
The initial reactants in the above reaction (i.e., CO and H₂) can be produced by other reactions such as the partial combustion of a hydrocarbon derivative:



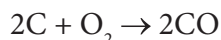
For example (when $n = 1$), methane (in the case of gas-to-liquids applications):



Or by the gasification of any carbonaceous source, such as biomass and, in the current context, carbonaceous waste:



The energy needed for this endothermic reaction is usually provided by (exothermic) combustion with air or oxygen:



A modification of this concept involves the proposed addition of addition of hydrogen from a carbon-free energy source, such as solar or nuclear power, during the gasification step. The theoretical concept is a hybrid process insofar as liquid hydrocarbon fuels are proposed to be produced from biomass wherein biomass is the carbon source and hydrogen is supplied from carbon-free energy. The modeling of this biomass-to-liquids process indicates that the concept has the potential to provide the transportation sector for the foreseeable future, using the existing infrastructure.

In addition, although not mentioned because the concept is modeled on the complete gasification of the feedstock, the addition of hydrogen will not only suppress the formation of carbon dioxide but also the formation of other by-products, thereby increasing the efficiency of the process. The presence of hydrogen will also reduce the amount of char and tarry by-products which is in complete agreement with the observed beneficial effect of hydroprocesses in crude oil refineries has been known for decades. The hydrogen and energy balance may be even better if water (also produced during gasification) could be used as the hydrogen source.

The pyrolysis of waste tires is also a source of liquid fuels; the process by which this is achieved is often called *thermal depolymerization*. This term, however, is more of a term of convenience since it is rare that depolymerization, in the true scientific sense, actually occurs. Thermal depolymerization (TDP) is a term that is used to describe the reduction of complex organic materials into lower-molecular-weight products. Nevertheless, in this context, thermal cracking and catalytic cracking as used in the crude oil industry are examples of thermal depolymerization. The feedstocks for such processes may also include non-oil-based waste products, such as old tires, offal, wood, and plastic. However, the so-called thermal depolymerization process does not in any way mimic the natural geological processes thought to be involved in the production of fossil fuels, such as crude oil and natural gas.

In the thermal depolymerization process, conversion efficiencies can be high but are feedstock dependent. Quantifying the potential amount of product (e.g., biodiesel) can be done on a feedstock carbon vs. product carbon basis, but such estimates are only approximate.

Quantifying the amount of oil which could be produced from tire pyrolysis can be done in a similar manner to quantifying the amount of biodiesel produced from waste vegetable oil. It is simply a case of equating the amount of waste product available to the production yields. In the case of tire pyrolysis, the number of used tires produced each year is well documented. What is less certain, however, is the amount of suitable road transport oil that can be yielded from the pyrolysis process itself.

Another source of waste for the production of liquid fuels is waste cooking oil; usually, biodiesel is the desired product. In fact, waste cooking oil is a valuable asset for conversion to liquid fuels and the quantity of biodiesel which could be produced from waste cooking oil can be quantified in a manner similar to that of biodiesel produced direct from agriculture. The only difference is that rather than calculating crop yields, it is necessary to quantify the amount of waste oil available.

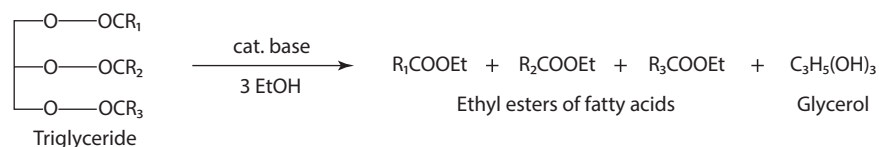
Biodiesel is a light-colored-to-dark-yellow-colored liquid that is immiscible with water and has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of approximately 150°C (300°F), making it non-flammable. Biodiesel has a density of 0.88 g/cm³. Biodiesel has a viscosity similar to crude oil-derived diesel (also known as petrodiesel, which is the current term to differentiate the different forms of diesel) and can be used as an additive in formulations of diesel to increase the lubricity of ultra-low sulfur diesel (ULSD) fuel. Much of the world uses a system known as the “B” factor to state the amount of biodiesel in any fuel mix – for example, fuel containing 20% v/v biodiesel is labeled B20 whereas pure biodiesel is referred to as B100.

Biodiesel is a renewable fuel that can be manufactured from algae, vegetable oils, animal fats, or recycled restaurant greases; it can be produced locally in most countries. It is safe, biodegradable, and reduces air pollutants, such as particulates, carbon monoxide, and hydrocarbon derivatives. Blends of 20% biodiesel with 80% crude oil-based diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems. Biodiesel is an alternative to crude oil-based diesel, but it is produced from biodegradable materials and can be used as fuel in diesel engines. It can also be used in boilers or furnaces designed to use heating oils or in oil-fueled lighting equipment or used neat (100% v/v biodiesel), or it can be blended with crude oil diesel.

Biodiesel is made by chemically reacting vegetable oil or animal fat (or combinations of oils and fats) with alcohol (usually nearly pure methanol or ethanol) and a catalyst (sodium hydroxide). The chemical reaction converts constituents of the vegetable oil into an ester (*biodiesel fuel*) and glycerol. Since the biodiesel is less dense than the glycerol, it floats on top of the glycerol and may be pumped off, or the glycerol can be drained off the bottom. The fuel can then be filtered and used in heating or lighting applications. It is possible to use the product in diesel engines without further processing, but caution is advised because of the potential for engine damage and it is recommended that impurities (unreacted alcohol and sodium hydroxide) are removed by washing.

Almost any variety of oil or grease (from new food-grade vegetable oil to used cooking oil or trap grease to wastewater treatment-plant grease) can be converted turned into biodiesel. However, the amounts of reactants (oil, methanol, and sodium hydroxide) vary to some degree, depending on what oil is used. The amount of methanol and sodium hydroxide must be sufficient to react with the vegetable oil, but excessive amounts of these reactants should not be used. Just as an engine requires excess air to be sure that all the fuel burns, it takes excess methanol to be sure all of the oil reacts.

The chemistry of biodiesel production (transesterification) involves the reaction of a glyceride-containing plant oil with a short chain alcohol such as methanol or ethanol:



Animal and plant fats and oils are typically made of triglyceride derivatives which are esters of free fatty acids with the trihydric alcohol, glycerol. In the transesterification reaction, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. Usually, this reaction will proceed either exceedingly slowly or not at all. Heat, as well as an acid or base, is used to help the reaction proceed more quickly.

Almost all biodiesel is produced using the base-catalyzed technique as it is the most economical process requiring only low temperatures and pressures and producing over 98% conversion (provided the starting oil is low in moisture and free fatty acids). The major steps required to synthesize biodiesel are: (i) purification, (ii) neutralization, (iii) transesterification, and (iv) workup.

In the purification step, if waste vegetable oil is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. The crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration, but the viscosity of the oil may not allow the drying agent to mix thoroughly.

The neutralization step is the removal of free fatty acids: A sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity (in moles) of base required to neutralize the acid is then calculated.

The transesterification step is the addition of bases in which a slight excess of the base is factored in to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide) is added slowly to the alcohol, and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess is added to drive the reaction to completion. The solution of sodium hydroxide in the alcohol is then added to a warm solution of the waste oil, and the mixture is heated (typically 50°C) for several hours (4 to 8

typically) to allow the transesterification to proceed. A condenser may be used to prevent the evaporative losses of the alcohol. Care must be taken not to create a closed system which can explode.

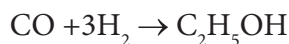
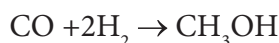
Once the reaction is complete, workup begins. The glycerol should sink, but when ethanol is used, it is reported that an emulsion often forms. This emulsion can be broken by standing, centrifugation, or the addition of a low-boiling (easily removed) non-polar solvent, decanting, and distilling. The top layer, a mixture of biodiesel and alcohol, is decanted. The excess alcohol can be distilled off, or it can be extracted with water. If the latter, the biodiesel should be dried by distillation or with a drying agent.

Ethanol is produced from organic feedstocks, such as biomass, by a fermentation process. However, recent efforts have focused on the production of ethanol from waste materials using a gasification process. The overall process consists of a thermo-chemical conversion of synthesis gas which is then converted to higher-molecular-weight alcohols by a catalytic process after which high purity ethanol is separated by distillation. The process is similar to modern-day methanol and gas-to-liquids processes. The key differentiating factors are the catalysts and their operating parameters.

Most current research efforts have centered on bacteria, enzyme, and acid/solvent hydrolysis fermentation-based ethanol production. However, the action of bacteria and enzymes is often very dependent on the feedstock. In addition, these processes generate a small quantity of ethanol over a period of days and the dilute aqueous ethanol product must be distilled to recover the ethanol. In the gasification-synthesis process, various carbonaceous feedstocks can be used, with appropriate modifications in the syngas production step.

A new system for converting trash into ethanol and methanol could help reduce the amount of waste piling up in landfills while displacing a large fraction of the fossil fuels used to power vehicles in the United States. The technology developed does not incinerate refuse, so it does not produce the pollutants that have historically plagued efforts to convert waste into energy. Instead, the technology vaporizes organic materials to produce synthesis gas that can be used to synthesize a wide variety of fuels and chemicals. In addition to processing municipal waste, the technology can be used to create ethanol out of agricultural biomass waste, providing a potentially less expensive way to make ethanol than current corn-based plants.

The new system makes synthesis gas in two stages. In the first stage, waste is heated in a 1,200°C (2,190°F) chamber into which a controlled amount of oxygen is added to partially oxidize carbon and free hydrogen. Not all of the organic material is converted and some forms of char which is then gasified when researchers pass it through arcs of plasma. The remaining inorganic materials, including toxic substances, are oxidized and incorporated into a pool of molten glass which hardens into a material that can be used for building roads or discarded as a safe material in landfills. The second stage is a catalyst-based process for converting synthesis gas into equal ethanol and methanol.



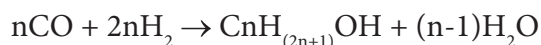
It is fairly common knowledge that the alcohols other than methanol and ethanol can be made from organic materials by fermentation. There is, however, a potential for the production of alcohols from organic waste.

Historically, the production of methanol, ethanol, and higher molecular alcohols from syngas has been known since the beginning of the last century. There are several processes that can be used to make mixed alcohols from synthesis gas including iso-synthesis, variants of Fischer-Tropsch synthesis, oxo-synthesis involving the hydroformylation of olefins, and homologation of methanol and lower-molecular-weight alcohols to make higher alcohols. However, in the context of the Fischer-Tropsch process, depending on the process and its operating conditions, the most abundant products are usually methanol and carbon dioxide but methanol can be recycled to produce higher-molecular-weight alcohols.

With the development of various gas-to-liquids processes, there was general recognition that higher-molecular-weight (higher-boiling) alcohol derivatives were by-products of these processes when catalysts or conditions were not optimized. Modified Fischer-Tropsch (or methanol synthesis) catalysts can be promoted with alkali metals to shift the products toward higher alcohols. Synthesis of higher-molecular-weight alcohols is optimal at higher

temperatures and lower space velocities compared to methanol synthesis and with a hydrogen/carbon monoxide ratio of approximately 1 rather than 2 or greater.

The first step in the synthesis to ethanol and higher alcohols is the formation of a carbon-carbon bond. Linear alcohols are then produced in stepwise fashion:

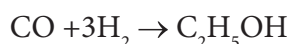
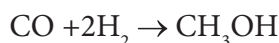


Stoichiometry suggests that the carbon monoxide/hydrogen ratio is optimum at 2, but the simultaneous presence of water-gas shift leads to an optimum ratio closer to 1.

As in other synthesis gas conversion processes, the synthesis of higher-molecular-weight alcohols generates significant heat, and an important aspect is choice of the proper reactor to maintain even temperature control which then maintains catalyst activity and selectivity. In fact, the synthesis of higher-molecular-weight alcohols is carried out in reactors similar to those used in methanol and Fischer-Tropsch synthesis. These include shell and tube reactors with shell-side cooling, trickle-bed, and slurry bed reactors.

Catalysts for the synthesis of higher-molecular-weight alcohols generally fall mainly into four groups: (i) modified high-pressure methanol synthesis catalysts, such as alkali-doped $\text{ZnO/Cr}_2\text{O}_3$, (ii) modified low-pressure methanol catalysts, such as alkali-doped Cu/ZnO and $\text{Cu/ZnO/Al}_2\text{O}_3$, (iii) modified Fischer-Tropsch catalysts, such as alkali-doped $\text{CuO/CoO/Al}_2\text{O}_3$, and (iv) alkali-doped sulfides, such as mainly molybdenum sulfide (MoS_2).

In the process, the feedstock enters the process and is converted to synthesis gas with the desired carbon monoxide/hydrogen ratio, which is then reacted, in the presence of a catalyst, into methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and higher-molecular-weight alcohols.



The catalytic synthesis process makes several different alcohols depending, in part, on residence time in the reactor and the nature of the catalyst. The alcohols can be separated by distillation and dried to remove water.

Another aspect of this concept is to produce the alcohols by a catalytic method in which the catalyst is in the form of unsupported nano-sized particles or supported on a high surface area support such as carbon, alumina, or silica (Mahajan and Jackson, 2004). In either arrangement, the nano-sized catalyst is suspended in an inert solvent, such as a high-molecular-weight hydrocarbon solvent, to form a slurry. The synthesis gas is then passed through the catalyst slurry to produce alcohols in the product stream. The operating temperature range is from 200°C to 300°C at a pressure ranges from 500 to 3,000 psi.

A further aspect of the waste-to-alcohols concept is the use of a plasma field (<http://www.fuelfrontiers.com/technology.htm>) in which temperatures are reputed (but not yet proved) to reach 30,000°C (54,000°F). The feedstock can be materials such as waste coal, used tires, wood wastes, raw sewage, municipal solid wastes, biomass, discarded roofing shingles, coal waste (*culm*), and discarded corn stalks. The plasma field breaks down the feedstock into their core elements in a clean and efficient manner.

Solid Fuels

The use of organic waste as cooking fuel in both rural and urban areas is not new. In 17th century England, the rural poor often burned dried cow dung because of the acute shortage of wood fuel due to widespread deforestation. In some countries, cattle and buffalo dung is still used as relatively good cooking fuel. In the beginning of the nineteenth century, sawdust briquettes were made with binding materials such as tar, resins, and clay bind the small particles together. None of these processes attained great importance because of their relatively high costs compared to wood and conventional charcoal fuels.

Fuel briquettes emerged as a significant business enterprise in the 20th century. In the 1950s, several economic methods were developed to make briquettes without a binder. A multitude of factories throughout the world produced literally tens of millions of tons of usable and economic material that met the household and industrial energy

needs. During the two World Wars, households in many European countries made their own briquettes from soaked waste paper and other combustible domestic waste using simple lever-operated presses. Modern industrial briquetting machines, although much larger and more complex, operate on the same principle, and a variety of solid fuels are available.

For over 100 years, informal waste collectors in Cairo have separated and dried organic waste products for sale as solid fuel for domestic use. This process faded somewhat when fossil fuel sources became available. Switching to conventional fuels may prove advantageous to those who can afford them, but given the economic and energy conditions in many cities, urban and agricultural wastes remain a viable alternative fuel.

Briquetting is undergoing resurgence, principally due to the convergence of three critical factors. First, the recent developments in briquette processing and binding have dramatically changed the economics of using fuel briquettes as an energy resource. Secondly, a shortage of fuel wood has become increasingly severe in most of the developing countries. Finally, there has been a steady increase by environmental concerns to address the problem of domestic and urban waste disposal, a dilemma that briquetting can help remedy.

Generally, briquette manufacture (*briquetting*) involves the collection of combustible materials that are not usable as such because of their low density, and compressing them into a solid fuel product of any convenient shape that can be burned like wood or charcoal. Thus, the material is compressed to form a product of higher bulk density, lower moisture content, and uniform size, shape, and material properties. Briquettes are easier to package and store, cheaper to transport, more convenient to use, and their burning characteristics are better than those of the original organic waste material.

The raw material of a briquette must bind during compression; otherwise, when the briquette is removed from the mold, it will crumble. Improved cohesion can be obtained with a binder but also without, since under high temperature and pressure, some materials such as wood bind naturally. A binder must not cause smoke or gummy deposits, while the creation of excess dust must also be avoided. Two different sorts of binders may be employed. Combustible binders are prepared from natural or synthetic resins, animal manure, or treated, dewatered sewage sludge. Non-combustible binders include clay, cement, and other adhesive minerals. Although combustible binders are preferable, non-combustible binders may be suitable if used in sufficiently low concentrations. For example, if organic waste is mixed with too much clay, the briquettes will not easily ignite or burn uniformly. Suitable binders include starch (5 to 10% w/w) or molasses (15 to 25% w/w) although their use can prove expensive (Lardinois and Klundert, 1993). It is important to identify additional, inexpensive materials to serve as briquette binders in Kenya and their optimum concentrations. The exact method of preparation depends upon the material being briquetted as illustrated in the following three cases of compressing sugar bagasse, sawdust, and urban waste into cooking briquettes.

Surplus bagasse presents a disposal problem for many sugar factories. Briquetting technology remains simple, and involves the following steps: (i) size reduction in which the bagasse is chopped, rolling, or hammered, (ii) drying in which moisture is removed by open air drying or by using forced, heated air in a large rotating drum, (iii) carbonization in which the bagasse is combusted in a limited supply of oxygen in a buried pit or trench until it carbonizes into charcoal, (iv) feedstock preparation in which the carbonized bagasse is mixed with a binder such as clay or molasses, (v) compaction and extrusion in which the material is passed through a machine-operated or manually-operated extruder to form *rolls* of charcoal, (vi) drying in which the rolls are air-dried for 1 to 3 days, causing them to break into chunks, and (vii) packaging in which the briquettes are made ready for sales.

Sawdust is waste material from all types of primary and secondary wood processing. Between 10 and 13% w/w of a log is reduced to sawdust in milling operations. Sawdust is bulky, and is therefore expensive to store and transport. Also, the calorific value of sawdust is quite low, so that briquetting is an ideal way to reduce the bulk, to increase the density, and thus to increase the calorific value. The equipment required for producing sawdust briquettes consist of a drier, a press, and an extruder with a tapered screw and a large revolving disk.

Sawdust briquettes are formed under sufficiently high pressure to produce cohesion between wood particles. In the process, the lignin softens and binds the briquette, so no additional binder is required. The use of sawdust briquettes has several advantages, including (i) price which is usually approximately the same as fuel wood but is much more convenient to use as they do not require further cutting and chopping, (ii) good burning characteristics in any kind of solid fuel stove and boiler, (iii) quick ignition followed by clean burning and only leaving 1% to 6% w/w ash, (iv) sulfur-free and burn without producing an odor, and (v) a heat content of approximately 18,000 KJ/kgm which is almost equivalent to the heat content of medium-quality coal.

Solid waste disposal is one of the most serious urban environmental problems in developing countries. Many municipal authorities collect and adequately dispose (in places other than landfill sites) less than half of these wastes. This failure is attributed to (i) an inadequate number of landfill sites, (ii) a variety of environmental regulations, (iii) the absence of sufficient capacity for waste processing and recycling, and last, but not least, (iv) the planned obsolescence of packaging and many of the items that form the basis of the waste.

Open or crude dumping is the most common method used by municipal authorities. Waste poses a health hazard when it lies scattered in the streets and at the dumping sites. It is now an accepted environmental philosophy that wastes have value and should be utilized based on principles of *reduce, reuse, recover*, and *recycle*. Through recycling, urban wastes can be transformed into useful products. Waste paper and leaves, in particular, provide a potentially important, alternative source of cooking fuel.

Waste – Hazardous

The types of hazardous wastes consist of solid, liquid, and gaseous streams and can be further classified as: (i) inorganic or organic waste, (ii) metal or non-metal waste, (iii) aqueous or non-aqueous waste, (iv) halogenated or non-halogenated waste, (v) ignitable or non-ignitable waste, (vi) corrosive or non-corrosive waste, (vii) reactive or non-reactive waste, and (viii) toxic or non-toxic waste.

Many hazardous materials can display more than one of the above properties, and their waste streams become more complex through mixing and contamination as they pass further from the place at which they were generated. It is much simpler to recover materials for reuse when they have not been cross-contaminated with other hazardous wastes or for that matter any other wastes. Therefore, it is usually desirable to set up, recovery, and recycling equipment as near the waste generation site as possible and in any case to segregate waste streams to prevent cross-contamination.

Some waste streams are clearly not compatible and should not be mixed unless special safety precautions have been taken to protect against the hazards generated by the mixing. An example of such incompatible waste streams is provided by an aqueous acid stream and a second stream containing either soluble sulfides or cyanides. Mixing would generate extremely toxic hydrogen cyanide (HCN) gas or hydrogen sulfide (H_2S) gas. Such incompatible waste streams usually involve corrosive or reactive wastes as one of the waste streams.

Waste separation processes are classified as (i) homogeneous processes or (ii) heterogeneous processes.

Many waste streams are homogeneous and require more complex processes such as distillation, extraction, and adsorption for recovery of valuable materials. On the other hand, heterogeneous wastes are usually relatively easy to separate into their respective phases, as is often the case with oily wastewaters, and the recovery of valuable materials can be quite convenient by the use of coalescing and settling devices.

The hazardous contaminants waste gas streams can be gases, liquids, or solids and must be removed from the gas stream prior to discharge to the atmosphere. Typical examples of hazardous gases are toxic materials such as carbon monoxide (CO), hydrogen sulfide (H_2S), and hydrogen cyanide (HCN), as well as environmentally undesirable gases such as oxides of nitrogen (NOx) and oxides of sulfur (SOx) as well as vapors from hazardous liquids such as paint solvents, gasoline, and halogenated cleaning solvents.

The liquids in gases are generally in the form of mists or fogs either caused by entrainment from gas-liquid contacting or by condensation of vapors in the gas stream due to cooling. The separation of mists and fogs requires coalescence of the liquid droplets into larger drops that can be more readily removed from the gas phase by settling.

Finally, the solids are usually in the form of dusts entrained in the gas stream and exist in the gas stream as a second phase, as with liquids in gases, they are also separated by mechanical techniques. Large particles can be readily settled out of a gas phase, but dust-like particles generally require some form of mechanical help. This mechanical help can take the form of cyclones, filters, scrubbers, or electrostatic precipitators, and all are in common use.

When gases exist as a separate phase in liquids, they can usually be recovered by coalescing the entrained gas bubbles into large bubbles and letting them settle out of the liquid phase. If necessary, the viscosity of the continuous liquid phase can be reduced by heating to improve both coalescing and settling. On the other hand, if the gases are dissolved in the liquid phase, some sort of carrier phase must be generated to strip the dissolved gases out of the liquid. This can be an inert gas, such as steam, air, carbon dioxide, or nitrogen, blown through the liquid phase as a stripping gas in a stripping column. Alternatively,

vapors generated from the liquid by heating it to a boil as in flash distillation can be used to strip out gases. In this latter case, the stripping gases are the vapors generated by the boiling liquid.

As with gaseous contaminants, liquid contaminants can also exist in liquid systems as either a separate liquid phase or as a homogeneous solution. When a heterogeneous system is encountered, the recovery processes are mechanical in nature such as settling, flotation, coalescing, cycloning, and centrifuging. On the other hand, if the system is homogeneous, either equilibrium- or rate-controlled processes must be used. The equilibrium processes are distillation, stripping, adsorption, extraction and supercritical extraction, ion exchange, and solvent precipitation.

Solid contaminants can also exist in liquids either as slurries or in the dissolved e. As with other heterogeneous systems, the slurries are separated by mechanical techniques such as settling, filtration, flocculation, flotation, centrifuging, and drying. With the homogeneous systems, evaporation and crystallization are frequently used to generate a heterogeneous system followed by one of the techniques for heterogeneous systems.

Solids can be contaminated with relatively small amounts of adsorbed gases liquids as with spent adsorbents, or with larger amounts of liquids as with cakes and sludges. Furthermore, solids can absorb either liquids or gases give swollen solids and gels. Solid polymers can show this latter behavior, and solids can exist as mixtures with other solids as in the case of many domestic and industrial solid wastes.

Most of the separation processes encountered in hazardous waste management involve processes such as batch distillation, adsorption, settling, and filtration which can be operated efficiently over a wide range of operating parameters. It is important to have this capability, particularly for continuous processes such as wastewater treating and stack gas scrubbing where flow rates change in response to manufacturing operations.

See also: Gas Cleaning, Recovery Processes.

Waste to Energy

Waste to energy (WTE or WtE or Energy from Waste, EfW) is the term used to describe the conversion of waste by-products into useful steam or steam-generated electricity. Typically, waste-to-energy is produced by converting municipal solid waste (MSW), which is defined as residential and commercial refuse, and makes up the largest source of waste in industrialized countries. This industry has been producing heat and power in the United States for a century, and there are currently in excess of one hundred waste-to-energy plants nationwide. Recently, however, the definition of waste has been expanded from municipal solid waste to include wastes such as wood, wood waste, peat, wood sludge, agricultural waste, straw, tires, landfill gases, fish oils, paper industry liquors, railroad ties, and utility poles.

Most waste-to-energy processes produce electricity and/or heat directly through combustion, or produce a combustible fuel commodity, such as methane (CH_4), methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), or synthetic fuels. The generation of energy by the use of many forms of waste can make a significant contribution to a national renewable energy. For example, incineration, the combustion of organic material such as waste with energy recovery, is the most common waste-to-energy implementation. Modern incineration plants are vastly different from old types, some of which neither recovered energy nor materials. Modern incinerators reduce the volume of the original waste by 95 to 96%, depending upon composition and degree of recovery of materials such as metals from the ash for recycling.

Generally, waste-to-energy facilities can be divided into two process types: (i) mass burn and (ii) refuse-derived fuel (RDF). Mass burn facilities process raw waste that has not been shredded, sized, or separated before combustion, although large items such as appliances and hazardous waste materials and batteries are removed before combustion. In mass burn systems, untreated municipal solid waste is combusted burned, with the heat produced converted into steam, which can then be passed through a steam turbine to generate electricity or used directly to supply heat to nearby industries or buildings.

Refuse derived fuel is a result of processing municipal solid waste to separate the combustible fraction from the non-combustible constituents, such as metals and glass. Refuse-derived fuel is mainly composed of paper, plastic, wood, and kitchen or yard wastes, and has a higher energy content than untreated municipal solid waste, and, like municipal solid waste, the refuse-derived fuel is then burned to produce steam and/or electricity. A benefit of using refuse-derived fuel is that it can be shredded into uniformly sized particles or compressed into briquettes, both of

which facilitate handling, transportation, and combustion. Another benefit of refuse-derived fuel rather than raw municipal solid fuels is that fewer non-combustible constituents such as heavy metals are burned.

The benefits of converting waste to energy include the following: (i) preventing the release of greenhouse gases such as methane into the atmosphere which would occur if the waste was sent to a landfill site, (ii) reducing the impact on landfill sites by reducing the volume of the waste 80 to 90%, (iii) providing an alternative to coal use, which prevents the release of emissions such as nitrogen oxides into the atmosphere, and (iv) saving the natural resources of the Earth by using less natural gas, crude oil, or coal for electricity generation.

Among the criticisms of the generation of energy via many wastes (even including biomass waste), biomass waste is the emission of fine particulate matter. Incineration of waste in general also has the complications of emission of heavy metals, trace dioxin, and acid gas, and critics argue that incinerators destroy valuable resources and they may reduce incentives for recycling.

Waste – Toxicity

With few exceptions, the constituents of petroleum, petroleum products, and the various emissions are hazardous to health. There are always exceptions that will be cited in opposition to such a statement, the most common exception being the liquid paraffin that is used medicinally to lubricate the alimentary tract. The use of such medication is common among miners who breathe and swallow coal dust every day during their work shifts.

Another approach is to consider petroleum constituents in terms of transportable materials, the character of which is determined by several chemical and physical properties (i.e., solubility, vapor pressure, and propensity to bind with soil and organic particles). These properties are the basis of measures of leachability and volatility of individual hydrocarbons. Thus, petroleum transport fractions can be considered by equivalent carbon number to be grouped into thirteen different fractions. The analytical fractions are then set to match these transport fractions, using specific *n*-alkanes to mark the analytical results for aliphatic compounds and selected aromatic compounds to delineate hydrocarbons containing benzene rings.

Although chemicals grouped by transport fraction generally have similar toxicological properties, this is not always the case. For example, benzene is a carcinogen but many alkyl-substituted benzenes do not fall under this classification. However, it is more appropriate to group benzene with compounds that have similar environmental transport properties than to group it with other carcinogens such as benzo(a)pyrene that have different environmental transport properties.

Nevertheless, the consultation of any reference work that lists the properties of chemicals will show the properties and hazardous nature of the types of chemicals that are found in petroleum. In addition, petroleum is used to make petroleum products, which can contaminate the environment.

The range of chemicals in petroleum and petroleum products is so vast that summarizing the properties and/or the toxicity or general hazard of petroleum in general or even for a specific crude oil is a difficult task. However, petroleum and some petroleum products, because of the hydrocarbon content, are at least theoretically biodegradable, but large-scale spills can overwhelm the ability of the ecosystem to break the oil down. The toxicological implications from petroleum occur primarily from exposure to or biological metabolism of aromatic structures. These implications change as an oil spill ages or is weathered.

Air emissions include point and non-point sources. Point sources are emissions that exit stacks and flares and, thus, can be monitored and treated. Non-point sources are fugitive emissions which are difficult to locate and capture. Fugitive emissions occur throughout refineries and arise from the thousands of valves, pumps, tanks, pressure relief valves, and flanges. While individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources.

The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping, can be potential sources of SO_x, NO_x, CO, particulates, and hydrocarbon emissions. When operating properly and when burning cleaner fuels such as refinery fuel gas, fuel oil, or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significant.

The majority of gas streams exiting each refinery process contain varying amounts of refinery fuel gas, hydrogen sulfide, and ammonia. These streams are collected and sent to the gas treatment and sulfur recovery units to recover the refinery fuel gas and sulfur. Emissions from the sulfur recovery unit typically contain some H_2S , SO_x , and NO_x . Other emission sources from refinery processes arise from periodic regeneration of catalysts. These processes generate streams that may contain relatively high levels of carbon monoxide, particulates, and volatile organic compounds (VOCs). Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon monoxide boiler to burn carbon monoxide and any volatile organic compounds, and then through an electrostatic precipitator or cyclone separator to remove particulates.

Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SO_x emissions limits of the United States Clean Air Act and to recover saleable elemental sulfur. Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units, and hydroprocessing units can contain high concentrations of hydrogen sulfide mixed with light refinery fuel gases. Before elemental sulfur can be recovered, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulfide. This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent. The solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbents such as molecular sieves, activated carbon, iron sponge, and zinc oxide are also used. In the amine solvent processes, DEA solution or another amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulfide is dissolved in the solution. The fuel gases are removed for use as fuel in process furnaces in other refinery operations. The amine-hydrogen sulfide solution is then heated and steam stripped to remove the hydrogen sulfide gas.

The current methods for removing sulfur from the hydrogen sulfide gas streams are typically a combination of two processes: the Claus Process followed by the Beavon Process, SCOT Process, or the Wellman-Lord Process. The Claus process consists of partial combustion of the hydrogen sulfide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur.

Most refinery process units and equipment are sent to a collection unit called the blowdown system. Blowdown systems provide for the safe handling and disposal of liquid and gases that are either automatically vented from the process units through pressure relief valves, or that are manually drawn from units. Recirculated process streams and cooling water streams are often manually purged to prevent the continued buildup of contaminants in the stream. Part or all of the contents of equipment can also be purged to the blowdown system prior to shut down before normal or emergency shutdowns. Blowdown systems utilize a series of flash drums and condensers to separate the blowdown into its vapor and liquid components. The liquid is typically composed of mixtures of water and hydrocarbons containing sulfides, ammonia, and other contaminants, which are sent to the wastewater treatment plant. The gaseous component typically contains hydrocarbons, hydrogen sulfide, ammonia, mercaptans, solvents, and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulfur oxides when flared.

Many of the gaseous and liquid constituents of the lower-boiling fractions of petroleum and also in petroleum products fall into the class of chemicals which have the one or more of the following characteristics are considered to be hazardous by the Environmental Protection agency in terms of the following properties (i) ignitability-flammability, (ii) corrosivity, (iii) reactivity, and (iv) hazardous.

See also: Beavon Process, Claus Process, Gas Cleaning, Tail Gas Cleaning, SCOT Process, Wellman-Lord Process.

Waste – Types

Waste types associated with petroleum refining typically include VOCs (volatile organic compounds), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH_3), hydrogen sulfide (H_2S), metals, spent acids, and numerous toxic organic compounds. Sulfur and metals result from the impurities in crude oil. The other wastes represent losses of inputs and final product. These pollutants may be discharged as air emissions, waste water, or solid waste. All of these wastes are treated. However, air emissions are more difficult to capture than wastewater or solid waste. Thus, air emissions are the largest source of untreated wastes released to the environment.

More specifically to petroleum and petroleum products, the alkanes in gasoline and some other petroleum products are CNS depressants. In fact, gasoline was once evaluated as an anesthetic agent. However, sudden deaths, possibly as a result of irregular heartbeats, have been attributed to those inhaling vapors of hydrocarbons such as those in gasoline.

Alkanes of various types of crude oils and various petroleum products were biodegraded faster than the *unresolved fractions*. Different types of crude oils and products are biodegraded at different rates in the same environments. An oil product is a complex mixture of organic chemicals and contains within it less persistent and more persistent fractions. The range between these two extremes is greatest for crude oils. Since the many different substances in petroleum have different physical and chemical properties, summarizing the fate of petroleum in general (or even a particular oil) is difficult. Solubility-fate relationships must be considered.

The relative proportion of hazardous constituents present in petroleum is typically quite variable. Therefore, contamination will vary from one site to another. In addition, the farther one progresses from lighter toward heavier constituents (the general progression from lower-molecular-weight to higher-molecular-weight constituents), the greater the percentage of polynuclear aromatic hydrocarbons and other semi-volatile constituents or non-volatile constituents (many of which are not so immediately toxic as the volatiles but which can result in long-term/chronic impacts). These higher-molecular-weight constituents thus need to be analyzed for the semi-volatile compounds that typically pose the greatest long-term risk.

In addition to large oil spills, petroleum hydrocarbons are released into the aquatic environments from natural seeps as well as non-point source urban runoffs. Acute impacts from massive one-time spills are obvious and substantial. The impacts from small spills and chronic releases are the subject of much speculation and continued research. Clearly, these inputs of petroleum hydrocarbons have the potential for significant environmental impacts, but the effects of chronic low-level discharges can be minimized by the net assimilative capacities of many ecosystems, resulting in little detectable environmental harm.

Short-term (acute) hazards of lighter, more volatile and water-soluble aromatic compounds (such as benzenes, toluene, and xylenes) include potential acute toxicity to aquatic life in the water column (especially in relatively confined areas) as well as potential inhalation hazards. However, the compounds which pass through the water column often tend to do so in small concentrations and/or for short periods of time, and fish and other pelagic or generally mobile species can often swim away to avoid impacts from spilled oil in open waters. Most fish are mobile, and it is not known whether or not they can sense, and thus avoid, toxic concentrations of oil.

However, there are some potential effects of spilled oil on fish. The impacts to fish are primarily to the eggs and larvae, with limited effects on the adults. The sensitivity varies by species; pink salmon fry are affected by exposure to water-soluble fractions of crude oil, while pink salmon eggs are very tolerant to benzene and water-soluble petroleum. The general effects are difficult to assess and quantitatively document due to the seasonal and natural variability of the species. Fish rapidly metabolize aromatic hydrocarbons due to their enzyme system.

Long-term (chronic) potential hazards of lighter, more volatile, and water-soluble aromatic compounds include contamination of groundwater. Chronic effects of benzene, toluene, and xylene include changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system.

At the initial stages of a release, when the benzene-derived compounds are present at their highest concentrations, acute toxic effects are more common than later. These non-carcinogenic effects include subtle changes in detoxifying enzymes and liver damage. Generally, the relative aquatic acute toxicity of petroleum will be the result of the fractional toxicities of the different hydrocarbons present in the aqueous phase. Tests indicate that naphthalene-derived chemicals have a similar effect.

Except for short-term hazards from concentrated spills, BTEX compounds (benzene, toluene, ethyl benzene, and xylenes) have been more frequently associated with risk to humans than with risk to non-human species such as fish and wildlife. This is partly because plants, fish, and birds take up only small amounts and because this volatile compound tends to evaporate into the atmosphere rather than persisting in surface waters or soils. However, volatiles such as this compound have can pose a drinking water hazard when they accumulate in ground water.

Petroleum is naturally weathered according to its physical and chemical properties, but during this process, living species within the local environment may be affected via one or more routes of exposure, including ingestion, inhalation, dermal contact, and, to a much lesser extent, bioconcentration through the food chain. Aromatic compounds of concern include alkylbenzenes, toluene, naphthalenes, and polynuclear aromatic hydrocarbons (PNAs).

Moreover, both atmospheric and hydrospheric impacts must be assessed when considering toxic implications from a petroleum release containing significant quantities of these single-ring aromatic compounds.

Waste Disposal

Given the large amounts of waste produced in modern society, there is an obvious need for technology to reduce the amount of waste that is land filled or, worse yet, improperly disposed.

Waste disposal techniques have created subtle and yet serious environmental pollution havoc in many developing countries. This has led to the degradation of abiotic and biotic components of ecological systems. Poor industrial waste disposal systems as well as the indiscriminate and inappropriate domestic litter disposal habit have been identified and proved to be basic features in rural settlements, semi-urban areas, and urban centers of the developing world. These have seriously contributed to environmental pollution and ecological deterioration.

The major reasons for these adverse effects were identified to be inadequate information and insufficient modern waste disposal facilities. As a result, the use of simple, yet efficient and environmentally benign disposal techniques are required.

Waste management solutions must be financially sustainable, technically feasible, socially, legally acceptable, and environmentally friendly. The conventional landfill, incineration, composting, and ways of handling wastes are common as mature technologies for waste disposal. Traditionally, the most commonly used technologies for the treatment and valorization of the organic fraction of waste are composting and anaerobic digestion. The generation of organic solid waste worldwide is dramatically increasing each year. Most of the organic solid wastes are composed of agricultural waste, household food waste, human and animal wastes, etc. They are normally handled as animal feed, incinerated or disposed to landfill sites. Organic solid wastes are comprised of materials rich in proteins, minerals, and sugars that could be used in other processes as substrates or raw materials.

The problem of waste disposal can be alleviated, to some extent, by a variety of methods, such as (alphabetically): (i) acid hydrolysis, (ii) anaerobic digestion, (iii) briquetting, (iv) enzymatic hydrolysis, (v) gasification, (vi) incineration, and (vii) pyrolysis.

Waste Disposal – Acid Hydrolysis

Acid hydrolysis is the means by which cellulosic material can be converted to lower-molecular-weight products and thence to fuels.

Enormous amounts of inexpensive and renewable lignocellulose waste are generated each year from forestry and agricultural production. These include fruit processing residues, dairy industry wastes, corn and sugar by-products, and paper industry wastes. Lignocellulosic biomass can be converted to biofuels such as ethanol and hydrogen via simple sugars. Lignocellulose is a composite of cellulose fibres embedded in a cross-linked lignin-hemicellulose matrix. It gives structure and strength to plants. Although abundant, lignocellulosic waste is difficult to convert to fermentable sugars because of its complex chemical structure: its three major components (cellulose – crystalline and amorphous – hemicellulose, and lignin) must be processed separately.

Cellulose consists of linear, highly ordered chains of glucose and is one of the most abundant biopolymers on the Earth. When produced by plants, it has both highly amorphous regions containing large voids and other irregularities as well as tightly packed crystalline regions. It also accumulates in the environment because it is resistant to most forms of degradation.

Hemicellulose is a complex polymer of a variety of sugar derivatives and consists predominantly of six-carbon and five-carbon sugar derivatives. Lignin is a poly-phenolic polymer that fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components. It is covalently linked to hemicellulose and crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall, and by extension, the plant as a whole.

Because lignocellulosic biomass is so complex, it is difficult to use as a feedstock for biofuel. A variety of physical, chemical, and enzymatic processes have been developed to fractionate lignocellulose into the major plant components of hemicellulose, cellulose, and lignin. Ethanol is produced from lignocellulose via pre-treatment, hydrolysis,

fermentation, and distillation (Figure 10.1). The goal of pre-treatment is to increase the surface area of lignocellulosic material, making the polysaccharides more susceptible to hydrolysis, by separating the xylose and lignin from the crystalline cellulose. Pre-treatment must also avoid the degradation or loss of precious carbohydrates and avoid the formation of by-products that can inhibit subsequent steps.

Steam explosion involves saturation of the pores of plant materials with steam followed by rapid decompression. The explosive expansion of steam reduces the plant material to separated fibers, increasing the accessibility of polysaccharides to subsequent hydrolysis. Ammonia fiber explosion (AFEX) is similar to steam explosion except that liquid ammonia is used. It is very effective on agricultural residues but has not been successful in pre-treating woody biomass.

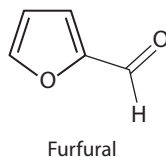
The mechanisms by which pre-treatments improve the digestibility of lignocellulose are not well understood. Pre-treatment effectiveness has been correlated with the removal of hemicellulose and lignin (lignin solubilization is beneficial for subsequent hydrolysis but may also produce derivatives that inhibit enzyme activity). Some pre-treatments reduce the crystallinity of cellulose, which improves reactivity, but this does not appear to be the key for many successful pre-treatments.

Hydrolysis is the use of water molecules to fragment a molecule. Hemicellulose is readily hydrolyzed to pentoses (5 carbon sugars), but pentoses are difficult to ferment. The cellulose hydrolyzes to hexoses (6 carbon sugars). Crystalline cellulose is difficult to hydrolyze, but the resulting hexoses are readily fermented. The three basic methods for hydrolyzing structural polysaccharides to fermentable sugars (glucose, xylose, arabinose) are concentrated acid hydrolysis, dilute acid hydrolysis, and enzymatic hydrolysis.

Acid treatment is the use of acid to hydrolyze cellulosic materials. Two acid processes hydrolyze both hemicellulose and cellulose with very little pre-treatment beyond comminution of the lignocellulosic material to particles of approximately 1 mm in size. These are concentrated and dilute acid hydrolysis.

Concentrated acid hydrolysis dissolves carbohydrates in woody biomass to form a homogenous gelatine with acid where cellulose is extremely susceptible to hydrolysis. Typically, this is achieved with 70 to 90% w/w sulfuric acid at room temperature, leaving lignin. Before fermentation, the solution of oligosaccharides is diluted to 4% sulfuric acid and boiled for four hours or processed using an autoclave at 120°C (250°F) for one hour to yield monosaccharides. Following neutralization with limestone, the sugar solution is fermented – the procedure takes 10 to 12 hours. Concentrated acid hydrolysis is attractive because it is relatively simple, and high sugar yields (approach 100% w/w of theoretical hexose yields in pure samples and 90% w/w of the theoretical yield in mixed samples which replicate municipal waste mixtures) are achieved.

Dilute acid hydrolysis (1% v/v acid by weight) greatly reduces the amount of acid required to hydrolyze lignocellulose. The process is accelerated at elevated temperatures: 100 to 160°C (212 to 320°F) for hemicellulose and 180 to 220°C (355 to 430°F) for cellulose. The high temperatures cause oligosaccharides released from the lignocellulose to decompose, greatly reducing yields of simple sugars to only 55 to 60% w/w of the theoretical yield. The decomposition products include toxins – such as acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, and furfural – which inhibit fermentation.



See also: Acid Hydrolysis.

Waste Disposal – Anaerobic Digestion

Anaerobic digestion (AD) focuses on hastening the natural process of biomass conversion to a gaseous fuel (biogas). Research has been conducted to ascertain optimal conditions for anaerobic digestion. These include (i) feedstock, (ii) nutrients, (iii) temperature, (iv) moisture, (v) pH, and (vi) atmospheric conditions. Most biomass waste feedstocks produce a biogas rich in methane. This medium to high Btu gas can, in some instances, be upgraded to a substitute natural gas (SNG). Depending on the feedstock, sulfur may also be produced.

During anaerobic digestion of biomass, a varied mixture of complex compounds is converted to a very narrow range of simple compounds, mainly methane and carbon dioxide. The anaerobic bacteria are responsible for the biochemical transformation of the biodegradable organic fraction (BOF). The AD of organic material basically consists of hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Figure 10.4). These chemical transformations are involved in the breakdown of complex polymers, such as cellulose, fats, and proteins to long and short chain fatty acids, and finally to methane, carbon dioxide, and water.

Anaerobic digestion is a complex process which requires strict anaerobic conditions [oxidation reduction potential (ORP) < -200 mV] to proceed and depends on the coordinated activity of a complex microbial association to transform organic material into mostly carbon dioxide and methane. Despite the successive steps, hydrolysis is generally considered as rate limiting. The hydrolysis step degrades both insoluble organic material and high-molecular-weight compounds (lipids, polysaccharides, proteins, and nucleic acids) into soluble organic substances (amino acids and fatty acids). The components formed during hydrolysis are further split during acidogenesis, the second step. Volatile Fatty Acids (VFAs) are produced by acidogenic bacteria along with ammonia (NH_3), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and other by-products. The 3rd stage in anaerobic digestion is *acetogenesis*, where the higher organic acids and alcohols produced by acidogenesis are further digested by acetogens to produce mainly acetic acid as well as carbon dioxide and hydrogen. The final stage of methanogenesis produces methane by two groups of methanogenic bacteria: the first group splits acetate into methane and carbon dioxide, and the second group uses H_2 as electron donor and carbon dioxide as acceptor to produce methane.

In a typical anaerobic digestion process, biomass is simply allowed to degrade in an anaerobic environment. A number of factors affect the entire process and include: (i) temperature of the substrate, (ii) loading rate, (iii) concentration of solids, (iv) reaction time, (v) pH, (vi) concentration of nutrients, and (vii) the presence of any toxic substances.

In terms of temperature, the optimal temperature (where digestion and gasification proceeds at the highest rate) is 35°C (95°F). Below 15°C (59°F), the rate is so slow that very little gas is produced. Temperature is also dependent on the bacterial populations: mesophilic or thermophilic. Mesophilic bacteria prefer temperatures ranging from 30 to 40°C (86 to 104°F). Thermophilic bacteria prefer temperatures ranging from 50 to 60°C (122 to 140°F). The loading rate is the amount of fermentable matter that is fed into the digester per cubic meter of digester capacity. Any change in loading rate affects the balance inside the digester, so it should be kept constant. For a given capacity, if the loading rate is increased, the fermentation period is correspondingly increased. The common range of solid concentration is 7 to 9% w/w. Digression from this range can cause fermentation to be retarded. The reaction time is the amount of time the fermentable material resides inside the digester. It has been observed that maximum gas production takes place within the first four weeks, and then gradually tapers off. Detention time can be significantly reduced if the temperature is raised or the contents of the digester are agitated, or the supply of nutrients in the digester is augmented.

Optimal gas formation occurs at pH of 7 to 8. If the pH becomes too acidic, gas production could stop altogether. Bacteria use nitrogen, phosphorus, and potassium for their nutrients. Once these are available, fermentation proceeds very quickly. Usually, some type of nutrient source is needed to help stimulate gas production. Toxic substances such as copper and its derivatives can inhibit gas production if found in large quantities. This is rare, however.

Essentially all organic material can be digested except for the stable woody materials since the anaerobic microorganisms are unable to degrade lignin. The biogas which is formed has a high CV and is considered as a renewable energy source. The main disadvantages of this process are (i) the possible presence of volatile siloxanes in the biogas that can cause serious damage in the energy users engine and boiler due to the formation of microcrystalline silica; and (ii) the increased concentration of heavy metals and various industrial “organics” in the residual sludge due to the significant reduction of the organic fraction during digestion, leaving the mineral and non-degradable fraction untouched.

Biogas can be used for electricity generation, combined heat and power (CHP), cogeneration, vehicle fuels (CNG), and production of liquid fuels. The liquid fuels would be low sulfur, low ash fuels that can be made for commercial use and easier to store, handle, and transport. Biogas can also be upgraded to pipeline quality for introduction into natural gas transmission lines and distribution to customers.

See also: Aerobic Digestion, Anaerobic Digestion.

Waste Disposal – Briquetting

Historically, briquettes (especially coal and coke briquettes) have been used for fuel for approximately one hundred years. However, with the advent of modern fuel systems, the use of briquettes use has declined and the use for these products is found most often in the operation of barbecue units. While still a marketable product for such use, briquettes as fuel (such as *smokeless fuel*) are not used often for domestic and industrial heating. Briquette manufacture (*briquetting*) involves the collection of combustible materials that are not usable as such because of their low density and compressing them into a solid fuel product of any convenient shape that can be burned. Using waste materials as a means to produce briquettes is investigated in this section.

Briquettes from waste materials are commonly made from a combustible material and binder. Combustible materials include char, low-grade biomass, and bagasse. Low-grade biomass includes grasses, weeds, thinning branches, forest waste resulting from logging, agricultural waste, sawdust, wood shavings, and leaves. A binding agent is usually necessary to increase the cohesion of the combustible materials. If the combustible material is not well-bound, the briquette will crumble when removed from the mold. The binding agents can include animal manure, treated and dewatered sewage sludge, starch, wax, clay, molasses, cement, wood pitch glue, and local plant resin or synthetic resin. A binder must not cause smoke or gummy deposits, and the creation of excess dust must also be avoided. For this reason, the use of non-combustible binding agents such as clay, cement, and other adhesive minerals are kept to a minimum. Typically, starch is used because it is relatively cheap and easily available. Since bagasse briquetting is often done on site or close to a sugar factory, molasses is usually the binding agent used for bagasse briquettes.

Briquette manufacture has six basic steps: drying of carbonaceous material, size reduction, mixing, briquetting, drying of briquettes, and packaging (Figure 10.5). For the manufacture of briquettes from bagasse, an additional step is necessary, and the order is a bit different: size reduction, drying of carbonaceous material, carbonization, mixing, briquetting, drying of briquettes, and packaging. The combustible material needs to be sufficiently dried so that it will burn evenly. Low-grade biomass needs to be sundried for 5 to 7 days. Usually, moisture is removed from bagasse by open air drying or by using forced, heated air in a large rotating drum.

The size of the material often needs to be reduced to a uniform size. This assists in uniform combining, briquetting, and burning. Char is finely crushed and passed through various screens to ensure small particle sizes. Bagasse is usually chopped, rolled, or hammered to produce small pieces.

In the carbonization step, bagasse is combusted in a limited supply of oxygen in a buried pit or trench until it carbonizes into charcoal. In the briquetting step, the mixture is tightly compacted through a manually operated or automatic press or extruder. The press or extruder for briquetting must be well-designed, strongly built, and capable of agglomerating the mixture sufficiently for it to be handled through the drying process. The extruder forms rolls of charcoal, while chunks of charcoal are produced using the press. On the other hand, sawdust briquettes are formed under sufficiently high pressure to produce cohesion between wood particles. Briquettes often need to be further dried after the briquetting step. Briquettes are dried in the sunlight approximately three days before use. Rolls of charcoal formed from extruders will break into chunks during the drying process.

Historically, briquettes and fuel wood were used until the development of crude oil-based energy. However, many developing countries were left behind in the energy revolution and continued to use plain char, home-made briquettes, or fuel wood. The combination of an exploding population and high rates of deforestation in developing countries have led to severe shortages of fuel wood. Because of improved processing and by using waste to produce briquettes, briquettes can be an economical option for fueling household energy needs in developing countries. Waste-derived briquettes burn and produce very little ash (<5% w/w) with little to no odor.

See also: Briquette, Briquette Manufacture.

Waste Disposal – Enzymatic Hydrolysis

Enzymatic hydrolysis was developed to better utilize both cellulose and hemicellulose from lignocellulosic materials. The enzymatic process must be preceded by extensive pre-treatment to separate cellulose, hemicellulose, and lignin. Because milder conditions are used compared to acid hydrolysis of cellulose, subsequent enzymatic hydrolysis of the

cellulose does not degrade pentoses during pre-hydrolysis. Cellulose is a homopolysaccharide of glucose linked by 1,4-glycosidic bonds. Enzymatic hydrolysis of cellulose proceeds in several steps to break glycoside-type bonds by the action of a system of enzymes known as cellulase. The system of enzymes also contains hemicellulase to hydrolyze any hemicellulose not solubilized by prehydrolysis. Unfortunately, enzymatic technologies are not likely to be suitable for unsorted municipal solid waste due to its high heterogeneity, and further research is necessary to convert wastes that are very high in hemicellulose.

In a fermentation process, glucose is fermented to produce a dilute ethanol-water solution (dilute beer). Xylose is difficult to convert to ethanol, but it does occur. Lignin, which is not susceptible to biological transformation, can be chemically upgraded or, more frequently, simply burned as boiler fuel.

Simultaneous saccharification and fermentation (SSF) has been developed for fermenting sugars released from lignocellulose. The process combines hydrolysis and fermentation to overcome end product inhibition. By combining hydrolysis and fermentation, glucose is rapidly removed before it can inhibit further hydrolysis. In the process, biomass feedstock is milled and then pre-hydrolyzed to yield a mixture of pentoses (xylose and arabinose) and fiber. The mixture is neutralized with limestone and mixed with cellulose and hemicellulose enzymes. The cellulose and any remaining hemicellulose are solubilized to hexose (glucose) and pentoses (xylose and arabinose), which are immediately fermented to ethanol. The optimum temperature for the hydrolysis/fermentation reaction is between the optimum temperature for cellulase activity and the best temperature for the yeast. Lignin is separated from the mixture and used as boiler fuel or converted to high-value octane enhancers that can be used as blend components to produce gasoline.

Distillation is a process such as when beer is distilled to ethanol. Energy consumption in the distillation process is partly responsible for criticism that ethanol production consumes more energy than it produces. Though there is basis for criticism in older plants, modern plants pay close attention to energy consumption. The ethanol produced is commercial-grade ethanol with all of the same expected properties and can be produced from a variety of waste materials.

There are several environmental considerations when using the acid hydrolysis process. In the process, water use is very high and, furthermore, when large amounts of acid are used, not only is corrosion and leakage of acid a problem, neutralization steps and chemicals are also needed. The process to collect, transport, and process wastes into ethanol is difficult. For best results, cellulose, hemicellulose, and lignin should be processed separately.

See also: Enzymatic hydrolysis.

Waste Disposal – Gasification

Gasification is a process that converts carbonaceous fuel into a combustible gas known as synthesis gas (CO and H₂) by partial combustion (oxygen-starved environment); the gas is nearly tar-free. Gasification is regarded as a key thermochemical conversion technology and offers the flexibility to be integrated into several industrial processes as well as power generating systems. Gasification compared to incineration has the added benefit that all of the organic material is fully converted to fuel for electricity generation or chemical production. Gasification systems have been reported to be more efficient for electricity generation when compared to incineration.

Gasification followed by synthesis to liquid fuels was first applied to coal in Germany during the 1920s, using technology developed by German researchers Franz Fischer and Hans Tropsch (the technology is now known as the Fischer-Tropsch process). During World War II, Germany, as well as Japan, produced diesel from coal, and South Africa later used coal-to-liquid (CTL) technology in response to international embargoes on crude oil. In principle, numerous process configurations exist for gasification products to fuels, depending upon the feedstock, gasifier type, the gas cleaning process, the product fuel, and whether electricity is cogenerated using part of the syngas output from the gasifier.

Agricultural, industrial, and urban waste has considerable promise as a feedstock for gasification because it contains relatively more lignin, which biological processes cannot convert. Unusable or low-value wastes such as furniture-making wood waste, beechwood, nutshells, olive husks, grape residues, bajra stalks, sweet sorghum stalks, bagasse, sugarcane leaves, sawdust, wood chips, corn cobs, nut shells, and rice hulls can be used as feedstock to produce high calorific value gas. Such waste is abundant in most developing countries and can be harnessed for

production of fuels and petrochemical intermediates. Knowing the potential of the waste for gasification and subsequent fuel production is essential for reducing pressure on traditional energy sources.

Gasification technology permits the production of syngas for fuel and chemical manufacture, and its application is mainly limited by gas quality (cleanliness). The research focus has been on reactor design, optimization of operating parameters, and addition of catalytically active materials to improve gas quality. Downstream clean-up of hot gas and catalytic tar conversion measures have been incorporated in modern technological designs. Gasification processes can be classified by (i) the Btu content of the product gas which can be high, medium, or low, (ii) the type of reactor hardware configuration such as single-stage design, multi-stage design, and molten salt batch reactor, as well as (iii) if the reactor is pressurized or not.

The heating value of the product gas is a function of the chemical composition, volatile constituents, and moisture content of the waste feedstock, and is carefully controlled given the application for the gas. Low Btu gas comprises a mixture of CO, H₂, and some other gases with a heating value in the range 11.15 MJ/m³ and limits its applicability to mainly chemical synthesis. Medium Btu gas consists of a mixture of methane (CH₄), carbon monoxide (CO), hydrogen (H₂), and various other gases with a heating value in the range 11.15 to 26.02 MJ/m³ and is primarily used in the synthesis of methanol, higher-molecular-weight hydrocarbon derivatives by way of the Fischer-Tropsch synthesis, and a variety of other chemicals. It can also be used as a fuel to generate steam or drive a gas turbine. The H₂-to-CO ratio in medium-Btu gas varies from 2:3 (CO-rich) to more than 3:1 (H₂-rich). The increased heating value is attributed to higher concentrations of methane and hydrogen as well as lower concentrations of carbon dioxide and the absence of nitrogen. High Btu gas consists predominantly of methane (>95% v/v) – it is compatible with natural gas and can be used as a synthetic or substitute natural gas NG (SNG).

In *single-stage* gasifiers, conversion takes place in a single reactor using steam, air, or oxygen. The common *single-stage technologies* are fixed bed, fluidized bed and entrained flow reactors. In fixed bed gasifiers, the fuel is fed from the top and the gasification medium is injected at the bottom. The fuel moves slowly down the reactor with the gas moving upwards in a countercurrent direction, whereas in co-current designs, the fuel and the gasification agent move in the same direction and the fuel must pass successively through the drying, pyrolysis, oxidation, and reduction zones. The advantage of countercurrent designs are fewer restrictions on fuel moisture and particle size, no special fuel preparation required, and a wide range of fuels can be used. By comparison, co-current gasifiers produce a better-quality gas but place strict requirements on fuel properties. Fluid bed gasifiers allow for more efficient gasification due to elimination of hot spots in the reactor. They are suitable for a wide range of feedstocks and can be scaled up to relatively large plants. They are more expensive to build and need better gas cleaning due to high particulate content in the product gas. Fluidized beds have no defined reaction zones, and the conversion of fuel and secondary pyrolytic reactions take place in the same volume. Tar conversion can be supported by introducing catalytically active bed materials.

The bed temperature is determined by the ash softening point and is usually in the range 815 to 1,040°C (1,500 to 1,905°F). Entrained flow gasifiers require pulverized fuels, and the fuels are introduced with the steam/oxygen feed and converted to gaseous products in a few seconds. Such gasifiers can be operated at lower temperatures (maintain ash as a dry solid) or at temperatures above the ash fusion temperature in a slagging mode (ash removed as a liquid). At higher temperatures, it is possible to produce a product gas which is virtually free from oil and tar. Although entrained flow gasifiers appear attractive for production of tar-free synthesis gas for petrochemical applications, challenges arise in achieving satisfactory size reduction (milling and grinding) of the waste. Single-stage gasifiers can be used for biomass and waste gasification if the requirements placed on product gas quality are low: direct co-combustion of hot raw gas or used as a fuel gas.

Various *multi-stage* processes are under development or in operation; they take into account the fuel conversion steps of drying, devolatilization, gasification, and combustion zones to enhance process efficiency and product gas quality by influencing and optimizing the operating parameters. These concepts are categorized as (i) single line, in which one mainstream of mass which pass through reactors arranged in series or (ii) double line, in which the mass mainstream is divided into at least two partial streams which pass through parallel arranged reactors. In the 'single line' process, fuel is dried and pyrolyzed in the first stage in an indirectly heated pyrolyzing unit.

The pyrolysis products undergo partial oxidation in the narrow zone between the pyrolyzer and the char gasifier. The product gas passes over the hot char bed and undergoes substantial tar cracking resulting in a higher-quality product gas. In the 'double line' process, combustion and gasification reactors are separate and are only connected by

heat transfer; a pyrolysis stage is used to split the fuel into char and gas. To provide the heat necessary for operation, the char or part of the pyrolysis gas must be oxidized outside the pyrolysis reactor.

When applied to biomass, a key advantage of gasification is that it can convert all of the organic matter into gases and then liquids, in particular lignin (component of lignocellulose resistant to enzyme attack) which is readily converted to gaseous products and made available as a fuel feedstock. Gasification of biomass from crop waste using a fluidized bed gasifier (565 to 750°C, 1,040 to 1,380°F) and an initial propane fuel source yields particulate, char, non-condensable gas, tar oil fraction, and an aqueous waste; a cyclone and a scrubber are used to condition the fuel gas.

Synthesis gas can be burnt to produce process heat and steam or used in gas turbines to produce electricity. Syngas can also be converted to a variety of fuels like hydrogen, methanol, or dimethyl ether (DME), as well as synthetic diesel and gasoline (via the Fischer-Tropsch process). Gasification followed by the Fischer-Tropsch synthesis has the potential to produce more fuel per ton of biomass.

Since the combustion of biomass imitates the natural process, the energy obtained does not add carbon dioxide to the environment. Incomplete combustion of biomass may produce organic particulate matter, carbon monoxide, and other organic acids. If high temperature combustion is used, nitrogen oxides can also be produced. The use of waste for such purposes also reduces the impact of methane emitted into the environment when organic waste decomposes in landfills. Some crop residues from conventional food crop harvests need to be left in the field to provide protection from erosion and to provide benefits such as micronutrient supplies, soil organic matter, and enhanced soil 'tilth' (the texture, structure, and pore spacing in soil).¹⁶ In cases where land is relatively flat and/or where conservation tillage methods are employed, a portion of the crop residues may be harvested for gasification. Establishment and communication of research-based guidelines are necessary to ensure that the removal of residue biomass for energy production is done in a sustainable manner.

The synthesis gas produced may contain tar, particulates, alkali compounds, and halogens that can clog filters, poison catalysts used in downstream fuel processing, or corrode the gas turbine used in electricity production. The availability of commercial quantities of waste feedstocks is another concern. Many residues have useful applications as fodder, fertilizer, and soil conditioner or as the raw material for a variety of products (particle board, medium-density fiber board (MDF), and recycled paper). In addition, availability is impacted by weather conditions (causing high and low production years in agriculture). Apart from availability, the market prices of biomass residues and waste generally depend upon a number of factors including (i) harvesting, (ii) collection and transport, (iii) market demand, (iv) local and international markets for various raw materials, and (v) the type of waste treatment technology deployed for the remaining material. The latter is particularly relevant when fees are charged to dispose of the waste, giving some organic waste streams a (theoretical) negative value.

See also: Gasification.

Waste Disposal – Incineration

Incineration is a controlled combustion process used for reducing solid wastes to carbon dioxide, water, flue gases, and ash. The ash residue may require disposal at a mono-fill or sanitary landfill given its toxicity, leaching potential, and contaminants. In addition, atmospheric emissions must be controlled to maintain good air quality. Not all solid waste can be incinerated; wastes such as white goods, industrial process waste, street and drain cleanings, and scrap steel cannot be fed to an incinerator and require alternative disposal methods. One of the most difficult aspects of waste as feedstock, whether for incineration or gasification, is its heterogeneous nature. Waste composition is influenced by numerous local conditions, such as population structure and local waste separation and recycling regulations. In addition, the composition of local waste is subject to major seasonal or even daily variations. The variability in chemical composition, water and ash content, heating value, and the presence of a number of substances, such as sulfur, chlorides, or metals, affect the performance of thermal conversion processes.

The basic technology for incineration plants was developed in Europe during the 1960s and 1970s. A major benefit of incineration is volume reduction of the original waste by 95 to 96%, thereby extending the life of landfill sites. Incineration is also used for the treatment of certain institutional wastes in niche areas as clinical wastes and certain hazardous wastes where pathogens and toxins can be destroyed by high temperatures.

Modern incineration plants reflect significant advances in addressing the technical and practical difficulties of material handling, combustion control, flue gas clean-up, and conformance with increasingly stringent air pollution control regulations. Energy recovery and production offer a direct economic benefit and lessen demands on processing and disposal requirements.

Incineration plants are usually classified as mass burn systems or refuse-derived fuel (RDF) systems and, together, account for 86 of the 98 currently operating waste-to-energy (WTE) facilities. Most mass burn systems burn waste in a single combustion chamber with excess air. The waste is burned on a sloping moving grate which helps agitate the municipal solid waste and mixes it with combustion air; many different proprietary grate systems exist. Grate design is critical because it must agitate the waste sufficiently to provide complete combustion and minimize ash carry-over in the flue gas which contributes to emissions. In the boiler/furnace portion of the incinerator, the waste characteristics of interest are the calorific value, moisture content, proportion of non-combustibles, and other components such as heavy metals, chlorine, and sulfur whose presence during combustion will result in the need for flue gas clean-up. The capacity of the furnace of the incinerator is approximately proportional to the calorific value of the waste. Mass burn produces by-products which have damaging consequences on the environment. Pollution control systems can be used to mitigate such risks. The technologies used to recover energy from municipal solid waste include (i) water-wall incineration and (ii) modular incineration.

Waterwall incineration involves the combustion of unprocessed municipal solid waste (mass burning) or processed municipal solid waste (refuse-derived fuel, RDF) in a furnace with integral boiler tubes. The advantages of water wall incineration are (i) pre-processing of waste is not required, except for large bulky items; (ii) the ash produced could be used for block manufacture, and (iii) auxiliary fuel is not required during normal steady-state operation. On the other hand, the challenges of water wall incineration are (i) complexity of operation, control and maintenance, and (ii) reserve furnace capacity is not available during downtime.

Modular incineration is used in smaller plants and is an assembly of prefabricated major components assembled in the field to form a total operation. Modular systems are similar to mass burn systems in that they combust unprocessed municipal solid waste, but they feature two combustion chambers and the municipal solid waste is charged into the system by a hydraulic ram and combustion takes place on a series of stationary hearths. Municipal solid waste is pushed from one hearth to the next by hydraulic rams. Two types of modular systems have been built and operated: starved air (slightly oxygen-deficient) and excess air (greater than stoichiometric). The advantages of modular incineration are the relatively low cost and shorter field construction time given their modular construction. The disadvantages of modular incineration are waste burnout is not always complete (increased ash quantities and reduced energy recovery); combustion control is less effective (possibility of discharge of trace organics); lower quality of equipment; and less redundancy than larger mass-fired water wall and refuse-derived fuel waste-to-energy (WTE) plants.

Feedstock preparation plays an important role in any thermal waste conversion approach. *Refuse-derived fuel* (RDF) is made when municipal solid waste is processed by mechanical means [picking, separation of inert materials (glass, minerals, ferrous and non-ferrous metals), flailing, screening, shredding, and conditioning] to produce a more homogenous material prior to incineration. Refuse-derived fuel systems utilize *pre-treated* municipal solid waste. Several types of refuse-derived fuel are made – coarse, fluff, powder, densified. They differ in complexity, power requirements, particle size, and whether the material is compacted into pellets or briquettes. Refuse-derived fuel can be used as the primary fuel source in a dedicated boiler or co-fired with a conventional fossil fuel as natural gas (NG) or landfill gas (LFG). The heating value of nearly all solid waste fuels is a function of carbon content. Ash content is generally low, but the amount of moisture is highly variable and depends upon moisture generation plus the effects of processing, handling, and storage.

Scrap tires can be processed into a waste-derived fuel (WDF) and mixed with other fuels without major alteration to the existing combustion facility. Tire-derived fuels (TDFs) are commonly used as supplemental fuel in cement kilns which are technologically and environmentally superior for selective waste disposal due to favorable internal kiln conditions as flame temperature (1,850°C, 3,360°F), residence time, alkaline environment, high gas turbulence, and mixing which ensure complete combustion, and the added benefit of having no bottom ash disposal problem since the residual materials (*e.g.*, steel from steel belted s) are incorporated into the clinker. The rationale behind the use of tire-derived fuel is as follows: (i) excellent combustion characteristics and high heating value, HHV, (ii) good availability, (iii) relatively low sulfur content, especially on a Btu basis, and (iv) reducing the environmental burden and health effects of tire stockpiles.

The full potential of incineration is not being realized because of widespread fears regarding environmental pollution. Modern incineration plants with adequate environmental safeguards and careful monitoring have been shown to be safe, and it is a technology that is likely to increase in importance during the next several decades. As environmental regulations continue to get stricter and the space for landfilling dwindles, production of refuse-derived fuels/waste derived fuels (RDF/WDF) holds promise from an energy content perspective (municipal solid waste is a renewable, abundant cheap resource) and because its conversion to energy alleviates disposal problems. The most publicized concerns related to the incineration of municipal solid waste involve the fear that it produces significant amounts of dioxin and furan emissions. Dioxin derivatives and furan derivatives are considered by many to be serious health hazards; thus, incineration for waste disposal and energy production remains a controversial topic for waste management.

See also: Incinerator.

Waste Disposal – Pyrolysis

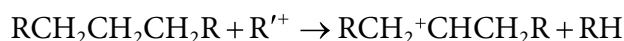
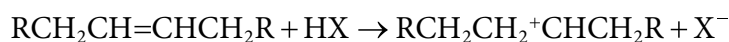
Pyrolysis is a thermochemical decomposition process involving the controlled burning or heating of a material carried out in the absence of oxygen, the product being synthesis gas, liquid, and char. In addition to liquid fuel or oil, pyrolysis generates a medium-BTU gas that after purification can be used as a fuel gas. Pyrolysis aims to convert waste into other valuable chemicals, which can be used as feedstock for downstream industrial processes or transportation fuels. In fact, all of the pyrolysis products have the potential of being fuels or intermediaries for producing other valuable products for the petrochemical industry.

Depending upon the operating conditions (temperature, heating rate, particle size, and solid residence time); pyrolysis can be divided into three subclasses: conventional, thermal or catalytic, fast or flash. For example, to maximize bio-oil production, fast/flash pyrolysis is used, heating the biomass to approximately 500°C (930°F) for less than ten seconds. In plastics pyrolysis, the macromolecular structures are broken down into smaller molecules (oligomers and monomers); further degradation depends on temperature, residence time, presence of catalysts, and other process conditions.

Molten salts such as lithium chloride-potassium chloride with 10% w/w cuprous chloride (LiCl-KCl-10% CuCl) at 520°C (970°F) are used to pyrolyze polymeric waste to yield a fuel oil. At a process temperature of 420°C (790°F), the gaseous fraction is minimized; this enables a higher liquid and solid fraction to be recovered. The recovered fractions consist of low-boiling oils, aromatics, paraffin waxes, and monomers.

Catalytic cracking involves a suitable catalyst to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. Catalytic degradation yields a narrow product distribution with a peak at lower boiling hydrocarbon derivatives and occurs at lower temperatures. Using solid acid catalysts, HZSM-5, HY, rare earth metal-exchanged Y-type (REY) zeolite, and silica-alumina for polymeric waste yield 30% v/v naphtha and 20% v/v high-boiling oil. The differences among catalysts arise in the production of coke and gas fractions. Formation of coke is not desirable as it results in catalytic deactivation by fouling and plugging the pore paths. Catalytic cracking, owing to its lower operating temperature, appears to be more technologically sound than thermal pyrolysis. The addition of a catalyst enhances the conversion and fuel quality, as compared to pure thermal pyrolysis.

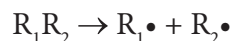
There are numerous proposed mechanisms for catalytic degradation. These include the carbonium ion mechanism and the free radical mechanism. In the carbonium ion (R^+) mechanism, there are four steps: (i) initiation, (ii) depropagation, (iii) isomerization, and (iv) aromatization. In the initiation step, the carbonium ion is generated through proton addition to an olefinic linkage, beta-scission, or through random hydride ion abstraction by low-molecular-weight carbonium ions:



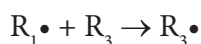
In the depropagation step, the molecular weight of the main polymer chain can be successively reduced through beta-scission. In the isomerization step, the carbonium ion intermediates can undergo hydrogen atom shift or carbon atom shift, leading to rearrangement of the molecules. Some of the carbonium ion intermediates can also undergo cyclization reactions, which leads to the formation of aromatics (aromatization step).

In the free radical mechanism, there are the three known radical mechanism steps: initiation, propagation, and termination. Normally, random bond breaking generates a radical (initiation). Then, the radical is propagated via a number of reactions such as beta-scission, radical abstraction, and radical decomposition (propagation step). Finally, recombination of two radicals leads to the termination step:

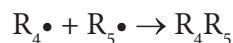
Initiation:



Propagation:



Termination:



Catalytic degradation of plastics is believed to have the greatest potential to be developed into a commercialized process. The oil produced in this process resembles the regular gasoline in all respects and reportedly gives better mileage as compared to commercial gasoline.

Thermal cracking (pyrolysis) involves the degradation of polymeric materials by heating in the absence of oxygen and is usually conducted between 350 to 900°C (660 to 1,650°F). The products formed are a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of paraffins, iso-paraffins, olefins, naphthenes, aromatics, and a non-condensable high calorific value gas. The thermal pyrolysis of polymeric waste at temperatures higher than 480°C (895°F) yields a gas-liquid hydrocarbon. At 650 to 760°C (1,200 to 1,400°F), more of the gaseous product is generated; conversely, at lower temperatures, up to 85% of the product is a liquid hydrocarbon.

The portion of each fraction and their precise composition depends primarily on the nature of the plastic waste and process conditions. Both the gaseous and liquid form of the polymeric waste can be utilized as a feed stream to petrochemical facilities. Generally, thermal cracking results in liquids with low octane value and high residue content at moderate temperatures; this is an inefficient process for producing gasoline ranges. The gaseous products obtained by thermal pyrolysis are not suitable for use as fuel products and require further refining to be upgraded to usable fuel products. A few researchers have sought to improve the thermal pyrolysis of waste plastics without employing the use of a catalyst.

Typically, discarded tires can be reduced in size by grinding, chipping, and pelletizing and passed through a classifier to remove the steel belting after which the chips are pyrolyzed for 1 hr at a temperature of 300 to 500°C (570 to 930°F) and then heated for 2 hours in a closed retort. The products are then distilled (purification and analysis); this yields oil and gas and char. However, discarded tires can also be shredded to 25 mm and ground to 24 mesh as a feed preparation step for occidental flash pyrolysis which involves flash pyrolysis and product collection. The pyrolytic reaction occurs without the introduction of hydrogen or using a catalyst. This yields a gaseous stream that is passed to a quench tower from which fuel oil and gas (recycled to char fluidized and pyrolysis reactor as a supplemental fuel) and carbon black (35% w/w) is produced.

Hydrothermal liquefaction and pyrolysis are often confused since both are thermochemical processes where organic compounds are converted to liquid products. However, in hydrothermal liquefaction, macro-molecules are

decomposed into unstable, reactive low-boiling molecules in the presence of a catalyst. These fragments repolymerize into high-molecular-weight oily compounds. The process involves solvolysis, decarboxylation, hydrogenolysis, and hydrogenation, leading to challenging mechanistic transformation studies. During solvolysis, the solvent reacts with the molecule, helping to begin the degradation of the biomass. Depolymerization of hemicelluloses, cellulose, and lignin further degrades the biomass to smaller molecules. In decarboxylation, loss of carbon dioxide can lead to rearrangement of the molecule. Molecules can also be further transformed via hydrogenolysis (water molecules split into H^+ and OH^- and react with molecules) and hydrogenation (H_2 is added to the molecule).

In proteinaceous wastes, proteins degrade to amino acids which can degrade into low-molecular-weight carboxylic acids. In cellulosic wastes, cellulose degrades into glucose by hydrolysis, which degrades into a number of aldehydes and ketones. These aldehydes and ketones can then be degraded to low-molecular-weight carboxylic acids also. Finally, plastic wastes such as PET, polypropylene, and polyethylene degrade into TPA, ethylene, and glycol. These degradation products can be further degraded to low-molecular-weight carboxylic acids also. The low-molecular-weight carboxylic acids can be converted to volatile carbon (carbon dioxide, carbon monoxide) and water.

The cellulose-based constituents of municipal solid waste are segregated and undergo a pyrolytic reaction at 116°C (240°F) and atmospheric pressure, yielding a liquid fuel ($\text{C}_6\text{H}_8\text{O}$, dependent on feedstock composition and reaction temperature).



For a pyrolytic reaction temperature of 500 to 900°C (930 to $1,650^\circ\text{F}$) and a pressure of 1 atmosphere, the products are solid, liquid, and gaseous fuels such as low-boiling oil (benzene), liquor (dissolved organics in water), and gas (town gas, manufactured gas, hydrogen, carbon monoxide, methane, volatile hydrocarbon derivatives). Municipal solid waste mixed with polyethylene chips and pyrolyzed at 100 to 400°C (212 to 750°F) at atmospheric pressure yielded similar products with lesser amounts of gas.

Pyrolysis products are used for electricity generation, heating, fuels (gaseous, liquid, solid), and feedstock to refineries for upgrade and petrochemical manufacture. Pyrolysis oils can be used in many applications, such as combustion in boilers, stationary diesel engines, industrial combustion turbines, and Stirling engines. The comparative option of upgrading these oils for vehicle engines does not appear promising. Conversion of industrial, urban, farm, agricultural, crop, and forestry waste to clean, sustainable energy is one of the major benefits of pyrolysis.

Several challenges must be overcome before pyrolysis can become a commercially viable means for energy production. Pyrolysis oils require downstream processing as they may contain char, alkali metals, 20 to 25% v/v water, as well as acid derivatives that are temperature sensitive and highly viscous which results in storage and engine problems.

Waste Management

The fuels production industry – including the non-renewable energy industry and the renewable energy industry – will increasingly feel the effects of the land bans on the hazardous waste management practices. Current practices of land disposal must change along with management attitudes for waste handling. The way refineries handle their waste in the future depends largely on the ever-changing regulations. Waste management is the focus, and reuse/recycle options must be explored to maintain a balanced waste management program. This requires that a waste be recognized as either *non-hazardous* or *hazardous*.

However, before a refinery can determine if its waste is hazardous, it must first determine that the waste is indeed a solid waste. In 40 CFR 261.2, the definition of solid waste can be found. If a waste material is considered a solid waste, it may be a hazardous waste in accordance with 40 CFR 261.3. There are two ways to determine whether a waste is hazardous. These are to see if the waste is listed in the regulations or to test the waste to see if it exhibits one of the characteristics (40 CFR 261).

There are four lists of hazardous wastes in the regulations. These are wastes from nonspecific sources (F list), wastes from specific sources (K list), acutely toxic wastes (P list), and toxic wastes (U list). And there are the four characteristics mentioned before: ignitability, corrosivity, reactivity, and extraction procedure toxicity. Certain waste

materials are excluded from regulation under RCRA. The various definitions and situations that allow waste to be exempted can be confusing and difficult to interpret. One such case is the interpretation of the *mixture* and *derived-from* rules. According to the mixture rule, mixtures of solid waste and listed hazardous wastes are, by definition, considered hazardous. Likewise, the *derived-from* rule defines solid waste resulting from the management of hazardous waste to be hazardous (40 CFR 261.3a and 40 CFR 261.1c).

There are five specific listed hazardous wastes (K list) generated in refineries. These are K048-K052. Additional listed wastes, those from nonspecific sources (F list) and those from the commercial chemical product lists (P and U lists), may also be generated at refineries. Because of the mixture and derived-from rules, special care must be taken to ensure that hazardous wastes do not *contaminate* non-hazardous waste. Under the mixture rule, adding one drop of hazardous waste in a container of non-hazardous materials makes the entire container contents a hazardous waste.

As an example of the problems such mixing can cause, consider the case with API separator sludge that is a listed hazardous waste (K051). The wastewater from a properly operating API separator is not hazardous unless it exhibits one of the characteristics of a hazardous waste. That is, the derived-from rule does not apply to the wastewater. However, if the API separator is not functioning properly, solids carry-over in the wastewater can occur. In this case, the wastewater contains a listed hazardous waste, the solids from the API sludge, and the wastewater would be considered a hazardous waste because it is a mixture of a non-hazardous waste and a hazardous waste.

This wastewater is often further cleaned by other treatment systems (filters, impoundments, etc.). The solids separating in these systems continue to be API separator sludge, a listed hazardous waste. Therefore, all downstream wastewater treatment systems are receiving and treating a hazardous waste and are considered hazardous waste management units subject to regulation. Oily wastewater is often treated or stored in unlined wastewater treatment ponds in refineries. These wastes appear to be similar to API separator waste.

Waste Management – Biological Methods

The purpose of a biological treatment system is to control the environment for microorganisms so that their growth and activity are enhanced, and to provide a means for maintaining high concentrations of the microorganisms in contact with the wastes. Thus, biodegradation is the use of living organisms (primarily microorganisms) to degrade pollutants previously introduced into the environment or to prevent pollution through treatment of waste streams before they enter the environment. Biological waste treatment is a generic term applied to processes that use microorganisms to decompose organic wastes either into water, carbon dioxide, and simple inorganic substances, or into simpler organic substances, such as aldehydes and acids. In the context of this book, biodegradation is the process of treating waste by biological methods while biodegradation is the outcome of the bioremediation process.

Biodegradation is emerging as one of several alternate technologies for removing pollutants from the environment, restoring contaminated sites, and preventing further pollution. On the other hand, biodegradation of waste is the conversion of waste chemicals by biological processes to simple inorganic molecules and, to a certain extent, to biological chemicals. The complete bioconversion of a substance to inorganic species such as carbon dioxide, ammonia, and phosphate (often referred to as mineralization).

Since biological treatment systems do not alter or destroy inorganic substances, and high concentrations of such chemicals can severely inhibit decomposition activity, chemical or physical treatment may be required to extract inorganic chemicals from a waste stream prior to biological treatment.

Detoxification refers to the biological conversion of a toxic substance to a less toxic species, which may still be relatively complex, or biological conversion to an even more complex chemical. An example of detoxification is the enzymatic conversion of paraoxon (a highly toxic organophosphate insecticide) to p-nitrophenol, which has only approximately 1/200 the toxicity of the parent compound.

Biodegradation is usually carried out by the action of microorganisms, particularly bacteria. However, microorganisms such as bacteria are not the panaceas for chemical wastes. Their function can vary depending upon the specific bacterium and the metabolic processes of the bacteria.

Biotransformation is the conversion of a substance through metabolism, thereby causing an alteration to the substance by biochemical processes in an organism. Metabolism is divided into the two general categories of catabolism, which is the breaking down of more complex molecules, and anabolism, which is the building up of life

molecules from simpler chemicals. The substances subjected to biotransformation may be naturally occurring or anthropogenic (made by human activities). They may consist of xenobiotic molecules that are foreign to living systems.

An important biochemical process that occurs in the biodegradation of many chemical waste chemicals is co-metabolism. This does not serve a useful purpose to an organism in terms of providing energy or raw chemical feedstocks to produce biomass, but occurs concurrently with normal metabolic processes. An example of co-metabolism of chemical waste is provided by the white rot fungus which degrades a number of kinds of organic chlorine compounds (including polychlorobiphenyl derivatives, cyanide derivatives, and chlorodioxin derivatives) under the appropriate conditions. The enzyme system responsible for this degradation is an enzyme that the fungus uses to break down lignin in plant material under normal conditions.

Biodegradation of chemical waste that can be metabolized takes place whenever the wastes are subjected to conditions conducive to biological processes. The most common type of biodegradation is that of organic compounds in the presence of air, that is, aerobic processes. However, in the absence of air, anaerobic biodegradation may also take place. Furthermore, inorganic species are subject to both aerobic and anaerobic biological processes.

Although biological treatment of chemical waste is normally regarded as degradation to simple chemical species such as carbon dioxide, water, sulfates, and phosphates, the possibility must always be considered of forming more complex (in some cases hazardous) chemical species. An example of the latter is the production of volatile, soluble, toxic methylated forms of arsenic and mercury from inorganic species of these elements by bacteria under anaerobic conditions.

Physical-chemical and biological treatment processes are employed as for wastewater treatment. In addition, chemicals are introduced for precipitation of nutrients, followed by coagulation and filtration for removing solids remaining after biological treatment. In some cases, granular activated carbon or membrane filtration (Noble and Stern, 1995) or a combination of membrane-assisted solvent extraction is used for additional purification of the groundwater streams and waste streams. This higher level of treatment is advisable because of the damage that any visual traces of chemical waste can do to the appearance of the waters. In addition, the treatment may combat the potential eutrophic effect that the nutrients phosphorus and nitrogen can have on the receiving water.

For the most part, anthropogenic compounds resist biodegradation much more strongly than do naturally occurring compounds. This is generally due to the absence of enzymes that can cause an initial attack on the compound. A number of physical and chemical characteristics of a compound are involved in its amenability to biodegradation. Such characteristics include hydrophobicity, solubility, volatility, and affinity for lipids. Some organic structural groups impart particular resistance to biodegradation. These structural groups include branched carbon chains, ether linkages, meta-substituted benzene rings, chlorine, amines, methoxy groups, sulfonates, and nitro groups.

Actinomycetes are microorganisms that are morphologically similar to both bacteria and fungi. They are involved in the degradation of a variety of organic compounds, including degradation-resistant alkanes and lignocellulose. Other compounds attacked include pyridine derivatives, phenol derivatives, non-chlorinated aromatic derivatives, and chlorinated aromatic derivatives.

Fungi are particularly noted for their ability to attack long-chain and complex hydrocarbon derivatives and are more successful than bacteria in the initial attack on polychlorobiphenyls. Phototrophic microorganisms, which include algae, photosynthetic bacteria, and cyanobacteria (blue-green algae) tend to concentrate organophilic compounds in their lipid stores and induce photochemical degradation of the stored compounds.

Usually, the products of biodegradation are molecular forms that tend to occur in nature and that are in greater thermodynamic equilibrium with their surroundings than the starting materials. Detoxification refers to the biological conversion of a toxic chemical to a less toxic chemical species.

Microbial bacteria and fungi possess enzyme systems required for biodegradation of wastes are usually best obtained from populations of indigenous microorganisms at a chemical waste site where they have developed the ability to degrade particular kinds of molecules. Although it has some shortcomings in the degradation of complex chemical mixtures, biological treatment offers a number of significant advantages and has considerable potential for the degradation of chemical wastes, even in situ.

The biodegradability of a compound is influenced by its physical characteristics, such as solubility in water and vapor pressure, and by its chemical properties, including molecular mass, molecular structure, and presence of various kinds of functional groups, some of which provide a “biochemical handle” for the initiation of biodegradation. With the appropriate organisms and under the right conditions, even substances such as phenol that are considered to be biocidal to most microorganisms can undergo biodegradation.

Properties of chemical wastes and their media can be changed to increase biodegradability. This can be accomplished by adjustment of conditions to optimum temperature, pH (usually in the range of 6 to 9), stirring, oxygen level, and the amount of the material. Biodegradation can be aided by removal of toxic organic chemicals and inorganic chemicals, such as ions of the heavy metal.

Aerobic processes for the treatment of waste utilize aerobic bacteria and fungi that require molecular oxygen. These processes are often favored by microorganisms, in part because of the high energy yield obtained when molecular oxygen reacts with organic matter. Aerobic and anaerobic digestion processes have been adapted to the use of an activated sludge process. These treatments can be applied to wastes such as chemical process wastes and landfill leachates. Some systems use powdered activated carbon as an additive to absorb nonbiodegradable organic wastes.

Anaerobic processes for the treatment of waste are those processes in which microorganisms degrade wastes in the absence of oxygen and can be practiced on a variety of organic wastes. Compared to the aerated activated sludge process, anaerobic digestion requires less energy, yields less sludge by-product, generates hydrogen sulfide which precipitates toxic heavy metal ions, and produces methane which can be used as an energy source.

Activated sludge is the biologically active sediment produced by the repeated aeration and settling of sewage and/or organic wastes. The dissolved organic matter acts as food for the growth of aerobic flora. These species produce a biologically active sludge which is usually brown in color and which destroys the polluting organic matter in the sewage and waste. The process is known as the activated sludge process.

Briefly, the activated sludge process is a versatile and effective waste treatment process. Microorganisms in the aeration tank convert organic material in wastewater to microbial biomass and carbon dioxide. Organic nitrogen is converted to ammonium ion or nitrate, and organic phosphorus is converted to orthophosphate.

The microbial cell matter formed as part of the waste degradation processes is normally kept in the aeration tank until the microorganisms are past the log phase of growth, at which point the cells flocculate and separate from the liquid. These solids settle out in a settler, and a fraction of them is discarded. Part of the solid the return sludge, is recycled to the head of the aeration tank and comes into contact with fresh sewage. The combination of a high concentration of microorganisms in the return sludge and a rich food source in the in-flowing sewage provides optimum conditions for the rapid degradation of organic matter.

However, in terms of pollution by humans, sewage sludge is not the beneficial organic fertilizer that many believe it to be. Sewage sludge spread on land may contaminate water by release of a variety of organic and inorganic contaminants. The spread of disease in ancient and medieval times due to contamination of water supplies will attest to this (Cartwright and Biddis, 1991). Similarly, chemicals leached from landfills by (acid) rain can also cause serious contamination of land and water systems. In addition, leachates from unlined pits and lagoons containing chemical liquids/sludge may pollute cause a specific pollution (drinking water) problem or a more general pollution problem.

Soil is a natural medium for a number of living organisms that may have an effect upon biodegradation of chemical wastes. Of these, the most important are bacteria. Wastes that are amenable to land treatment are biodegradable organic substances. However, in soil contaminated with chemical wastes, bacterial cultures may develop that are effective in degrading normally recalcitrant compounds through acclimation over a long period of time. Land treatment is most used for crude oil refining wastes and is applicable to the treatment of fuels and wastes from leaking underground storage tanks.

Land treatment can also be applied to biodegradable organic chemical wastes, including some organic halogen compounds. Land treatment is not suitable for the treatment of wastes containing acids, bases, toxic inorganic compounds, salts, heavy metals, and organic compounds that are excessively soluble, volatile, or flammable.

Bioreactors have been used for wastewater treatment processes for decades. The reactors may be either fixed film or slurry phase. Fixed film reactors are similar to the traditional trickling filters or rotating biological contactors (RBCs) of the wastewater industry. In either case, the microorganisms are supported on the medium of the filter. The

wastes are passed over the filter (or in the case of rotating biological contactors, the filter is passed over the waste) allowing the microorganisms to come into contact with the wastes and break down the organic chemical. Slurry phase reactors are tanks into which the wastes, nutrients, and microorganisms are placed. The tank is mixed and may be aerated. In many instances, contaminated groundwater is used to create the waste slurry. Both fixed film and slurry phase treatments are either batch or continuous mode.

Waste Management – Chemical Methods

The effects of chemical waste on the environment are reflected by the effects on organisms and effects on the overall ecosystem. It is also worth remembering that virtually all chemical wastes are harmful to humans, even poisonous, depending upon the amount ingested. As with all environmental pollutants, such chemical wastes eventually reach a state of physical and chemical stability and equilibrium with the environment, although it may take many centuries to occur. In many cases, the behavior (or reactivity) and ultimate fate of a chemical waste is a function of its physical properties and surroundings. On the basis that it is not possible to wait for the chemical to reach an equilibrium with its surroundings, methods of remediation are essential.

The first step in considering the appropriate technology to employ to treat a specific waste is to determine whether the waste is hazardous or nonhazardous. And the definition of a hazardous/nonhazardous waste is determined by the relevant legislation. There is the general tendency to think of a chemical waste as some obscure and ill-defined sludge discarded from a process. However, chemical waste can also be in the form of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), metals, radioactive chemicals, radioactively contaminated materials, or a mixture of any or all of these types.

The ideal treatment process reduces the quantity of chemical waste to a small fraction of the original amount and converts it to a nonhazardous form, if such a conversion is possible. Another consideration in selecting a treatment technology is the location where the wastes are to be treated. For example, wastes may be treated in place (in situ), within the confines of the site, or at an off-site facility (ex situ).

There are various alternative waste treatment technologies, such as chemical treatment and biological treatment. Chemical treatment process and physical treatment processes as well as thermal methods of treatment (including incineration) as well as solidification or stabilization are processes that are used to (i) destroy the waste by complete elimination of the chemical or (ii) by conversion of the chemical to a benign form and produce a final residual chemical that is suitable for disposal.

The effectiveness of the application of each of these technology groups to a specific waste varies depending on (i) the type of waste, (ii) the concentration of the individual components in the waste, (iii) the physical phase of the chemical, (iv) the desired level of treatment, and (v) the final method of disposal of any remaining residue. The waste characteristics can include such properties as volatility (gases, volatile chemicals in water, gases, or volatile chemicals adsorbed on solids, such as catalysts), liquid phase chemicals (such as organic solvents), dissolved or soluble chemicals (water-soluble inorganic species, water-soluble organic species, compounds soluble in organic solvents), semisolid chemicals (sludge, grease), and solid chemicals (dry solids, including granular solids with a significant water content, such as dewatered sludge, as well as solids suspended in liquids). Waste treatment may occur at three major levels: (i) primary waste treatment, (ii) secondary waste treatment, and (iii) tertiary waste treatment, sometimes referred to as polishing.

Primary waste treatment is generally regarded as preparation for further treatment, although it can result in the removal of by-products and reduction of the quantity and hazard of the waste. Secondary waste treatment detoxifies, destroys, and removes hazardous constituents. Tertiary waste treatment (polishing) usually refers to the treatment of a waste product for safe discharge. An example is the treatment of recycled water to remove any chemicals so that it may be safely discharged or repurposed.

Typically, chemical treatment processes alter the chemical structure of the constituents of the waste to produce either an innocuous or a less hazardous by-product. Chemical processes tend to produce minimal air emissions and can often be carried out on the site of the waste generator. In fact, some chemical waste treatment processes are available as mobile units.

The applicability of chemical treatment processes to waste management depends upon the chemical properties of the waste constituents and the products of the processes. Particularly relevant properties are (i) acid-base character, (ii) oxidation and/or reduction behavior, (iii) precipitation and/or the tendency to form complexes, (iv) flammability and combustibility, (v) reactivity and corrosivity, and (vi) compatibility with other chemical waste.

Waste Management – Physical Methods

In contrast to the chemical methods of waste treatment, physical processes for the treatment of chemical waste include processes that separate components of a waste stream or change the physical form of the waste without altering the chemical structure of the constituent chemicals.

These processes – which are based upon one or more of the physical properties of the released chemical – are particularly useful for separating hazardous chemicals from an otherwise nonhazardous waste stream so that they may be treated in a more concentrated form, separating various chemical components for different treatment processes, and preparing a waste stream for ultimate destruction in a biological or thermal treatment process. These processes include (i) phase separation (filtration), (ii) phase transfer (extraction, sorption), (iii) phase transition (distillation, evaporation, precipitation), and (iv) membrane separations (reverse osmosis, hyperfiltration, and ultrafiltration).

The important aspect of physical methods of remediation is to isolate the contaminant so that it can be recovered/destroyed while being contained within a specific area. In terms of containment, there are several technologies available which usually involve construction of a containment wall (usually concrete) around the contaminated area where the side where leakage into nearby water systems can occur. One aspect of remediation that is evolving is the application of soil-mix wall technology. This technology consists of mixing soil in situ with cement grout using multiple shaft augers to construct overlapped cement columns. The use of augers makes it possible to define the treatment zone clearly and to confine the contaminant(s).

Solidification and stabilization are treatment systems which move beyond the older concept of dig-and-move and are designed (i) to improve the handling and the physical characteristic of the waste, or (ii) or to decrease the surface area across which transfer or loss of contained pollutants can occur, (iii) or to limit the solubility of, or detoxify, any chemical constituents in the waste.

Stabilization/solidification processes are being used to minimize the potential for groundwater pollution from land disposal of hazardous wastes. Many variations are used, but most rely on pozzolanic reactions to chemically stabilize and physically solidify the waste. Portland cement alone or in combination with fly ash, cement kiln dust lime, or other ingredients is the principal solidifying agent used. The processes are effective for immobilizing any heavy metals present in sludge, contaminated soils, and other wastes. They are not as effective at immobilizing toxic organic chemicals. Organically modified clays are now being evaluated as an additive to stabilization and/or solidification processes in order to adsorb and retain these organic pollutants in the solidified waste form.

The environmental acceptability of stabilization and solidification processes depends on the long-term ability of the waste form to retain contaminants. This will be governed by the chemical binding mechanisms involved and by the durability of the waste form. Widespread acceptance of stabilization and solidification processes will be hampered until the long-term durability of the waste form can be demonstrated.

Stabilization usually involves the addition of materials (chemicals or derivatives thereof) that ensure that the chemical constituents are maintained in their least soluble or least toxic form. In the solidification process, the results are obtained primarily, but not exclusively, via the production of a monolithic block of treated waste with high structural integrity. Stabilization techniques limit the solubility of, or detoxify, the waste contaminants even though the physical characteristics of the waste may not be changed. Both of these techniques might also have been classified under phase transition or phase conversion.

Encapsulation, another perhaps more specific form of waste stabilization, is a method by which mixed wastes, i.e., waste containing radioactive chemicals and higher level radioactive waste can be rendered less harmful to the environment. The use of polyethylene, chosen for its durability, has been suggested as a suitable encapsulating agent.

Waste Management – Pretreatment

Dilute and non-toxic wastewaters are normally treated in a biological treating plant prior to disposal. However, when aqueous wastes are received from a variety of sources in a large industrial organization and treated in a common biological waste treating plant, some of these waste streams may be too toxic or too reactive to be acceptable as feeds to the biological treating plant. Furthermore, different waste streams may be incompatible due to potential chemical reactions between them which could release toxic gases to the atmosphere. This is particularly true of process wastewaters from the chemical process and metal finishing industries and for chemical wastes from laboratories. Such wastes must be pretreated to remove toxic metals or other toxic ions. They must also be brought to near neutral pH (approximately 7.0) before they can be sent to either an on-site or a publicly owned water treatment works.

The incompatibility of such waste streams is usually due to one stream containing a potentially toxic-forming material such as sulfide or cyanide anions and the other containing a reactive material, like strong acids, that can release toxic hydrogen cyanide (HCN) or hydrogen sulfide (H_2S) to the atmosphere. The examples of this type of incompatibility are (i) chromium- and cyanide-containing aqueous waste streams from metal finishing, where the acid pH needed to reduce chromium from the six-valence state to the three-valence state would release toxic hydrogen cyanide (gas), and (ii) highly basic streams and streams capable of releasing toxic vapors such as ammonia in the presence of bases.

Waste Management – Thermal Methods

Outside of the traditional containment methods (land filling and capping), the application of some type of thermal process has, until recently, been the most common form of treatment for chemical waste. Thermal treatment processes have lost some popularity recently due to the threat of emissions from incomplete combustion. Except for vitrification, thermal technologies are *ex situ* processes requiring the wastes to be transported to the processing unit. However, the use of a thermal destruction technology may be (depending upon the nature of the emissions) superior to wet scrubbing technologies for emissions cleaning.

Incineration is the controlled combustion of chemicals in an enclosed area. Thus, incineration of chemical waste and, for example, sewage sludge, is a process that involves exposure of the waste chemicals to oxidizing conditions at a high temperature, usually in excess of 900°C ($1,650^{\circ}\text{F}$).

Incineration of solid and liquid chemical wastes, such as polychlorobiphenyl derivatives, is a common and highly efficient method of destruction. The destruction of polychlorobiphenyls commences at ca. 800°C ($1,470^{\circ}\text{F}$) and commercial incinerators operate at temperatures in excess of $1,000^{\circ}\text{C}$ ($1,830^{\circ}\text{F}$). Suitable for the purpose are stationary incinerators, cement kilns, incinerator ships, and smaller mobile thermal destruction units.

This, of course, is a convenient point at which to note only one of the many ways in which environmental events on land, in the air, and in the water are connected. And the connection between the air, land, and water systems is not guaranteed to be sequential:

Land systems ↔ water systems ↔ atmosphere

Briefly, emissions from the incinerators may be gaseous (SO_x , NO_x , particulate matter) which can pollute the atmosphere or, through the formation of the constituents of acid deposition, the water systems and the land systems, and therefore control is necessary.

Alternatively, these emissions might have a direct effect on the vegetation by deposition of the gases or particulate matter directly on to the land at a point downwind of the incinerator. In addition, solid waste (ash) from an incinerator can pollute the land and, as a result of leaching by rain (acidic or otherwise), pollute the water systems. Therefore, attention must be focused on the disposal of the ash.

The air emission systems from these thermal reactors, as well as from the furnaces that burn solids emanating from wastewater plants, must be designed to prevent chemical and particulate air pollution. These air emission systems include electrostatic precipitators and afterburners. In addition, sulfur-containing fuels emit sulfur dioxide

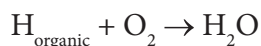
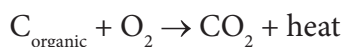
and other sulfur containing gases as a result of combustion and these sulfur-containing gases have the potential for conversion to sulfates (sulfuric acid in the atmosphere) which can be deposited on the land as sulfate.

Nitrogen oxides (also produced during fuel combustion) are converted to nitrates in the atmosphere, and the nitrates eventually are deposited on soil. Soil also adsorbs nitric oxide (NO) and nitrogen dioxide (NO₂) readily, and these gases are oxidized to nitrate in the soil. Carbon monoxide is converted to carbon dioxide and possibly to biomass by soil bacteria and fungi. Elevated levels of heavy metals (such as lead) from mines and smelters are also found on in the soil near such facilities.

Thermal treatment of chemical waste can be used to accomplish the common objectives of waste treatment which are (i) volume reduction, and (ii) removal of volatile, combustible, mobile organic matter and destruction of toxic and pathogenic chemicals. Incineration utilizes high temperatures, an oxidizing atmosphere, and often turbulent combustion conditions to destroy wastes.

The effective incineration of wastes depends upon the combustion conditions, which are (i) a sufficient supply of oxygen in the combustion zone, (ii) thorough mixing of the waste, the oxidant, and any supplemental fuel, (iii) combustion temperatures above 900°C (>1,650°F), and (iv) sufficient residence time to allow reactions to occur.

Usually, the heat required for incineration comes from the oxidation of organically bound carbon and hydrogen contained in the waste chemical or in supplemental fuel:



These reactions destroy organic matter and generate heat required for endothermic reactions, such as the breaking of C-Cl bonds in organic chlorine compounds.

Incineration detoxifies chemical waste by destroying organic compounds, reduces the volume of the waste, and converts liquid waste to a solid product by vaporizing any fluids present in the wastes. The primary use of incineration is for the destruction of volatile organic compounds and semi-volatile organic compounds. Incinerators have been extremely capable of destroying organic compounds in waste. Removal efficiencies as high as 99.9999% have routinely been achieved (often referred to as the six-9s treatment level).

Incineration systems are designed to accept specific types of chemicals which vary according to feed mechanisms, operating temperatures, equipment design, and other parameters. The main products from complete incineration include water, carbon dioxide, ash, and certain acids and oxides, depending upon the waste in question.

Waste incineration and pyrolysis processes typically include single-chamber liquid systems, rotary kilns, and fluidized-bed incineration systems. In a single-chamber liquid system, a brick-lined combustion chamber contains liquids that are burned in suspension. In addition to being the primary parts of an incineration system, these units can be used as afterburners for rotary kilns.

A rotary kiln is a versatile large refractory-lined cylinder capable of burning virtually any liquid or solid organic waste; the unit is rotated to improve turbulence in the combustion zone. Fluidized-bed incineration uses a stationary vessel within which solid and liquid wastes are injected into a heated, extremely agitated bed of inert granular material; the process promotes rapid heat exchange and can be designed to scrub off the gases.

The ideal wastes for incineration are predominantly organic chemicals that will burn with a heating value of at least 5,000 Btu/lb and preferably more than 8,000 Btu/lb. Such heating values are readily attained with waste having a high content of organic constituents. In some cases, however, it is desirable to incinerate wastes that will not burn alone and which require supplemental fuel, such as methane and crude oil liquids.

The examples of such wastes are nonflammable organic chlorine wastes, some aqueous wastes, or soil in which the elimination of a particularly troublesome contaminant is worth the expense and trouble of incinerating it. Inorganic matter, water, and organic heteroelement content of liquid waste is important in determining their susceptibility to incineration. Many wastes, including hazardous waste, are burned to produce fuel for energy recovery in furnaces and boilers. This process (co-incineration) uses combustible waste material more for energy generation than for waste destruction. In addition to heat recovery from combustible waste, an existing on-site facility, rather than a separate waste incinerator, can be used for waste disposal.

Incinerators can be designed to handle wastes in any physical state and have proven effective in treating solids, liquids, sludge, slurries, and gases. The effectiveness of an incinerator depends on three factors: (i) temperature of the combustion chamber, (ii) residence time in the chamber, and (iii) amount of mixing of the chemical with air while in the chamber.

Normal combustion temperatures range between 900 and 1,500°C (1,650 to 2,280°F); in some instances, the temperatures employed are much higher. Many incinerators for hard-to-burn compounds employ two combustion chambers. The first chamber converts the compounds to gas and initiates the combustion process. In the second chamber, combustion of the gases is completed.

There are four major components of chemical waste incineration systems: (i) preparation, (ii) combustion, (iii) pollutant removal, and (iv) ash disposal.

Waste preparation for liquid wastes may require filtration, settling to remove solid material and water, blending to obtain the most appropriate mixture for incineration, or heating to decrease viscosity. Solids may require shredding and screening. Atomization is commonly used to feed liquid wastes. Several mechanical devices, such as rams and augers, are used to introduce solids into the incinerator.

The inert portion of the waste remains as ash after incineration. For liquid waste, the amount of ash remaining is generally minimal, whereas for solid waste, the volume of ash can be as much as one-third by weight of the original material. If the ash contains metals or radioactive chemicals, it must be further treated prior to disposal. The most frequently employed method of treating the ash remaining from the incineration process is solidification/stabilization. The hot ash is often quenched in water, and, prior to disposal, it may require dewatering and chemical stabilization. A major consideration with waste incinerators and the types of wastes that are incinerated is the disposal problem posed by the ash, especially in respect to potential leaching of heavy metals.

Waste Management – Waste Exchange

Waste exchange takes advantage in an organized way of the concept that the waste held by one company may be a valuable resource for another company. In many cases, valuable materials can be recovered from waste streams, but the generator has no on-site opportunities to recycle or reuse this material. On the other hand, other divisions or units of the same company or outside companies may be purchasing this same material as a feedstock to their manufacturing operations. By selling the recovered material from the generating company to a user company at a price reflecting the savings to both companies insofar as (i) the seller does not have the expense of disposing of the material and (ii) the buyer has an economic incentive to use the recovered material rather than new material purchased in the open market.

The waste exchange concept can be an effective means for the “disposal” of laboratory chemicals that are no longer needed for the purpose for which they were originally purchased. Such chemicals may be chemicals that are unused after the completion of the project for which the chemicals were purchased and, therefore become part of a storage inventory for use at some unknown time in the future in which there are merely excess inventory.

However, if the chemicals are collected, labeled, and stored in the original containers in a convenient place accessible to potential users, they can be used by personnel other than the original purchasers in preference to making new purchases. However, this system does require a control system to provide assurance that identity and purity of the chemicals are correct and that unstable materials are not included in the chemical storage inventory.

Waste exchange between companies are usually worked out on single items which pose no threat to either company in terms of disclosure of trade secrets or proprietary process technology, or exposure to sanctions under anti-trust laws against cooperation. These factors along with the problems of negotiating equitable prices for recovered material as feeds tocks have prevented waste exchange between companies from achieving very much of its potential. The chemicals may also be offered for sale on the open market which can also apply not only to unused chemicals but also to chemicals recovered as by-products from waste streams generated in chemical manufacturing processes.

In spite of the potential obstacles to waste exchange that may arise, the concept has potential for waste minimization, and financial return should lead to increased application of this technique.

See also: Hazardous Waste, Waste.

Waste Minimization and Separation

Waste minimization has been defined as (i) source reduction, (ii) waste separation and concentration, (iii) reuse and recycling of components recovered from waste streams, and (iv) waste exchange.

Source reduction includes recycling of materials within a process, thus extending the life of the materials before disposal and as a result decreasing the amount of waste material generated. Typical operations falling into this category are (i) recycling of cutting oils in metal fabrication with chip removal by gravity or mechanical means, (ii) recycling of metal degreasing solvents with grease removal by distillation, and (3) recycling of dry cleaning solvents by distillation. Manufacturers of equipment for these operations often include the accessory equipment needed for recycling right in the process equipment package, thereby greatly extending the life of the necessary process fluids. When the sludge level in or the quality of the spent process fluids becomes too bad for "in process" recycling, the spent fluid can be removed from the process equipment and recovered for recycling in external on-site or off-site equipment. Thus, the only materials that must be finally discarded are the metal chips, sludges, and impurities recovered from the separation processes in the recycling circuits.

Waste separation and concentration describes the techniques used to recover valuable components from a waste stream in concentrations sufficiently high to make them useful as feedstocks. They could be sent back to the process from which they came or used as raw materials to other processes. In this latter case, they would be good candidates for a waste exchange where people operating different processes could trade raw materials recovered from wastes. In many cases, waste separation and concentration has a dual beneficial effect in that the removal of toxic materials from wastewater streams can make the wastewaters non-toxic and suitable for recycling or simple disposal. Thus, both the impurity and the wastewater may be recycled and removed from the hazardous waste definition.

Reuse and recycling refer to the recovery of useful material from a waste stream for reuse. This reuse can be either (i) recycling to the process it came from, assuming that the material can be recovered in sufficient purity or (ii) using the material for a less demanding purpose. For example, solvents used in the formulation of paints can be recovered by distillation and used for cleaning painting equipment. With a suitable purification process, they may even be suitable for recycling to the original use.

Waste exchange takes advantage in an organized way of the concept that one man's waste may be another man's valuable resource. In many cases, valuable materials can be recovered from waste streams, but the generator has no on-site opportunities to recycle or reuse this material. On the other hand, other divisions or units of the same company or outside companies may be purchasing this same material as a feedstock to their manufacturing operations. By selling the recovered material from the generating company to a user company at a price reflecting the savings to both companies, then (i) the seller doesn't have the expense of disposing of the material and (ii) the buyer gets some economic incentive to use the recovered material rather than new material purchased in the open market.

Waste exchanges can be effective for laboratory chemicals that are no longer needed for the purpose for which they were originally purchased. They may be leftovers from completed or terminated projects or merely excess inventory. If they are effectively collected, labeled, and stored in the original containers in a convenient place accessible to potential users, they can be used by personnel other than the original purchasers in preference to making new purchases. This system works well and saves money when used inside a single corporation having large laboratories. This is largely because there is no question about what company receives the financial benefits of the operation. However, it does require a control system to provide assurance that identity and purity of the chemicals are correct and that unstable materials are not included in the chemical storage inventory.

Waste exchanges between companies are usually worked out on single items which pose no threat to either company in terms of disclosure of trade secrets or proprietary process technology, or exposure to sanctions under anti-trust laws against cooperation. These factors along with the problems of negotiating equitable prices for recovered material as feedstocks have prevented waste exchange between companies from achieving very much of its potential. However, DuPont (1991) has offered a resolution to this problem by offering for sale in the open market chemicals recovered as by-products from waste streams generated in chemical manufacturing. This arm's length approach may be the direction that inter-company waste recycling takes in the future. In spite of the institutional obstacles to waste exchange, its great potential for waste minimization and financial return should lead to increased application of this technique.

Waste Streams

Waste streams are any unused solid or liquid by-products of a process, and they can also be exploited for ethanol production.

Waste streams are often inexpensive to obtain, and in many instances, they have a negative value attributable to current disposal costs. Some principal waste streams currently under consideration include mixed paper from municipal solid waste, cellulosic fiber fines from recycled paper mills, bagasse from sugar manufacture, corn fiber, potato waste, and citrus waste, sulfite waste liquors, and hydrolysis streams from fiber board manufacture. Each waste stream has its own unique characteristics, and they generally vary from one source or time to another.

Waste streams with low lignin content and smaller particle size are easier to deal with than those with higher lignin contents and larger particle sizes. Waste paper that has been treated by a chemical pulping process is much more readily converted than is native wood or herbaceous residue.

See also: Biomass Feedstocks, Municipal Solid Waste, Urban Waste, Waste.

Waste Tires

A waste tire (often referred to as a scrap tire) is a tire that is no longer mounted on a vehicle and is no longer suitable for use as a vehicle tire due to wear, damage, or deviation from the manufacturer's original specifications. A waste tire includes a repairable tire, scrap tire, and altered waste tire, but does not include a tire-derived product, crumb rubber, or a used tire that is organized for inspection and resale by size in a rack or a stack.

More specifically, a waste tire is a tire that is no longer mounted on a vehicle and is no longer suitable for use as a vehicle tire due to wear, damage, or deviation from the original specifications issued by the manufacturer. Therefore, a waste tire is a tire that is not brand new, nor is it mounted on a vehicle, and it is not stored in a manner for display and sale that allows for inspection of the tread. A waste tire is not intended for use on a vehicle again.

Tire recycling is the process of recycling waste tires that are no longer suitable for use on vehicles due to wear or irreparable damage. These tires are a challenging source of waste, due to the large volume produced, the durability of the tires, and the components in the tire that are ecologically problematic. Because tires are durable and non-biodegradable, they can consume valued space in landfills. Newer technology, such as pyrolysis and devulcanization, has made tires suitable targets for recycling despite their bulk and resilience. Aside from use as fuel, the main end use for tires remains ground rubber.

See also: Tires – Scrap.

Waste Vegetable Oil

Waste vegetable oil (WVO) is grease from the nearest fryer which is filtered and used in modified diesel engines, or converted to biodiesel through the process of transesterification and used in any old diesel car.

Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating in the world, this local solution does not scale well.

However, in an effort to reduce dependency on petroleum-based fuels, there is an interest in installing conversion kits which allow diesel engines to burn waste vegetable oil along with standard diesel or biodiesel fuel. Such vehicles are usually termed *grease cars*.

A grease car uses filtered vegetable oil, often obtained at little to no cost from local restaurants, to power a slightly modified diesel engine. The primary modifications made to a grease car are a new storage tank for the vegetable oil, additional fuel filters, and a heater to bring the oil up to operating temperature.

A grease car gets approximately the same mileage as a regular diesel car, and the emission levels are a marked improvement over other types of vehicles, making it a phenomenal tool for reducing pollution. Greenhouse gas

emissions can drop anywhere from 78 to 87% overall when you convert a diesel car to a grease car. While they still emit nitrogen oxides and carbon monoxide, grease cars are carbon neutral.

A grease car may also require standard diesel fuel during the start-up process since the vegetable oil may not readily ignite at lower air temperatures until warmed by a heater unit.

See also: Biomass, Grease Car, Vegetable Oil.

Water

Water (H_2O) is a polar inorganic compound that is (at room temperatures) a tasteless and odorless liquid which is almost colorless with a gentle suspicion of blueness. It is often considered to be a universal solvent because of the ability to dissolve many substances and is, therefore, also considered to be the *solvent of life*. In fact, natural water (i.e., water as it exists in nature) invariably includes various dissolved substances, and special process steps are required to obtain chemically pure water.

Water is the only common substance to exist as a gas (water vapor or steam), solid (ice), and liquid in normal terrestrial conditions. The addition or removal of heat can cause phase transitions such as freezing to a solid (liquid water to ice), melting (ice to liquid water), vaporization (liquid water to vapor), condensation (vapor to liquid water), sublimation (ice to vapor), and deposition (vapor to ice).

Water differs from most liquids in that it becomes less dense as it freezes. At 1 atmosphere pressure (14.7 psi), water reaches a maximum density of $1,000 \text{ kg/m}^3$ (62.43 lb/ft^3) at 3.98°C (39.16°F). The density of ice is 917 kg/m^3 (57.25 lb/ft^3) which represents an expansion on the order of 9% than can exert pressure on pipes. In a lake or ocean, water at 4°C (39°F) sinks to the bottom and ice forms on the surface and floats on the liquid water. This ice insulates the water below, preventing it from freezing solid which assists in the survival of aquatic organisms.

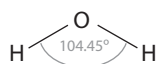
Overall, water is a unique chemical that is a major component of all living things and is anomalous in many of the chemical and physical properties (Eisenberg and Kauzmann, 1969.; Gerstein and Levitt, 1998; Sharp, 2001). Some of properties are essential for life, while others have effects on the size and shape of living organisms, how they work, and the physical limits or constraints within which they must operate. Moreover, many of the basic physical properties of water can be explained in molecular and structural terms which is relevant to the behavior of water as the properties pertain to the aquasphere. In particular, it is the readiness of water to particular in hydrogen bonding interactions (Eisenberg and Kauzmann, 1969., 1969; Gerstein and Levitt, 1998. Sharp, 2001).

Water is an important aspect of the Earth system and, like any of the components of the Earth system, can be polluted by any type of energy or energy source. It is, therefore, of necessity to know the properties of water in order to protect any of the water systems of the Earth.

The study of water (hydrology) is divided into a number of subcategories, the most prominent of which are (i) limnology, which is the branch of the science dealing with the characteristics of fresh water, including biological properties as well as chemical and physical properties, and (ii) oceanography, which is the science of the ocean and its physical and chemical characteristics.

Water is an inorganic, transparent, tasteless, and odorless chemical substance and is a major component of all living things, and it is anomalous in many of the physical and chemical properties. Some of the properties are essential for life, while other properties have significant (often detrimental) effects on the size and shape of living organisms, how the organisms work, and the constraints within which the organisms must operate. Many of unusual properties of water occur because of the attraction among its polar molecules. The properties of water include cohesion, adhesion, capillary action, surface tension, the ability to dissolve many substances, and high specific heat.

A water molecule is made up of two hydrogen atoms bonded to an oxygen atom (H_2O) and is often referred to as a bent molecule (in a tetrahedral configuration) in which each end of a water molecule has a slight electric charge giving the molecule polarity.



In some scientific circles, because of the tetrahedral configuration of the molecule, water has been jokingly referred to as tetrahedral soup.

This uneven distribution of charges (polarity) across a molecule makes one end positive (H) and the other negative (O). The positive hydrogen ends of one water molecule attract the negative oxygen ends of nearby water molecules causing them to associate, and this attraction causes water molecules to form temporary bonds (hydrogen bonds) that can break easily. Also, water is an amphoteric molecule insofar as it can exhibit the properties of an acid or a base, depending on the pH of the aqueous solution. Water readily produces both hydrogen ions (H^+) and hydroxyl ions (OH^-), and because of the amphoteric character nature, water undergoes self-ionization. The product of the concentrations of hydrogen ions and hydroxyl ions is a constant, so the respective concentrations of these ions are inversely proportional to each other.

The tendency for water molecules is to form weak hydrogen bonds (cohesion), and because of cohesion, water molecules remain joined together as they move within or between the cells of organisms. A special example of cohesion is surface tension which is the force that acts on the particles at the surface of a liquid. In liquid water, each water molecule is pulled in all directions by other water molecules, but at the surface of the water, the attractive force of other water molecules pulls only downward and sideways. This force causes molecules at the surface to be held more tightly together, forming a type of skin at the surface of the water. Small insects, such as water striders, can walk on water by taking advantage of this surface tension. Also, it is the surface tension that causes raindrops to form round beads when they fall onto a glass surface.

Water molecules are not attracted only to each other but have a tendency to associate with other substances through adhesion. Adhesion allows water to stick to the sides of blood vessels or to the vascular tubes in plants. Both cohesion and adhesion allow water to move in one continuous column from the roots to the leaves of a plant. This upward movement (capillary action) is the result of both cohesion of the water molecules to each other and adhesion to the sides of the glass. Capillary action is the combined force of attraction among water molecules and with the molecules of surrounding materials causing a liquid to climb upward against the force of gravity. Thus, capillary action allows water to move through materials with pores inside and also causes water molecules to cling to the fibers of material like paper and cloth.

Water is often referred to as the universal solvent because of the ability to dissolve more substances than any other known solvent. The main property of water that makes it such a good solvent is its polarity, and, as a result, the charged ends of the water molecule attract the molecules of other polar substances. (Like dissolves like.) Water can dissolve substances such as sugars (carbohydrates, $C_6H_{12}O_6$), bleach (sodium hypochlorite, $NaOCl$), and salt ($NaCl$). Water can also dissolve gases such as carbon dioxide (CO_2) and oxygen (O_2). Moreover, the ability of water to dissolve many substances allows water to deliver essential nutrients to cells in plants, animals, and other organisms. Water dissolves nutrients in food but does not dissolve nonpolar substances such as oil and wax which are water-repellant (hydrophobic).

Thus, water has a number of unique properties (Table W-3) that make it suitable for living organisms and a solvent for many materials. Thus, it is the basic transport medium for nutrients and waste products in life processes (Stollenwerk and Kipp, 1990). But, a point that must not be missed; there is also the very real potential for water to transport toxins.

Table W-3 General properties of water.

Property	Effects and significance
Excellent solvent	Transport of nutrients and waste products.
High dielectric constant	High solubility of ionic substances.
Maximum density at 4°C	Ice floats; vertical circulation restricted in stratified bodies of water.
High heat of evaporation	Determines transfer of heat and water molecules between the atmosphere and bodies of water.
High latent heat of fusion	Temperature stabilized at the freezing point of water.
High heat capacity	Stabilization of temperatures of organisms.

The high dielectric constant of water affects its solvent properties, in that most ionic materials are dissociated in water. In addition, water has a high heat capacity; thus, a relatively large amount of water is required to change appreciably the temperature of a mass of water. Hence, a body of water can have a stabilizing effect upon the temperature of nearby geographic regions.

The high heat capacity of water also prevents sudden changes of temperature in large bodies of water and thereby protects aquatic organisms from the shock of abrupt temperature variations. The high heat of vaporization of water (585 cal/g at 20°C, 68°F) also stabilizes the temperature of bodies of water and influences the transfer of heat and water vapor between bodies of water and the atmosphere.

Water has its maximum density at 4°C (39°F), a temperature above its freezing point (0°C, 32°F). The fortunate consequence of this fact is that ice floats, so that few large bodies of water ever freeze solid. Furthermore, the pattern of vertical circulation of water in lakes, a determining factor in the chemistry and biology of water, is governed largely by the unique temperature-density relationship of water. Thus, the physical condition of a body of water strongly influences the chemical and biological processes that can occur in water.

Surface water occurs primarily in streams, lakes, and reservoirs. Lakes may be classified as oligotrophic, eutrophic, or dystrophic, an order that often parallels the life of the lake (Table W-4).

Table W-4 General types of lakes.

Types of lakes	Description
Based on nutrients	
Oligotrophic lake	Low nutrient concentrations.
Eutrophic lake	Oversupply of nutrients like nitrogen and phosphorus; usually a result of agricultural run-off or discharge of municipal sewage.
Dystrophic lake	Low pH, high humic acid content, and brown waters.
Based on origin	
Volcanic lake	Receives water from magma after volcanic eruptions; has highly restricted biota.
Endemic lake	Very ancient, deep, and have endemic (native to that area) fauna.
Artificial lake	Created due to construction of a dam.
Based on of salinity	
Fresh water lake	Low concentration of salts.
Salt water lake	High concentration of salts.
Meromictic lake	Rich in salts; permanently stratified.
Desert salt lake	Occur in arid regions; high salt concentrations due to high evaporation.

Oligotrophic lakes are deep, generally clear, deficient in nutrients, and without much biological activity. Eutrophic lakes have more nutrients, support more life, and are more turbid. Dystrophic lakes are shallow, clogged with plant life, and normally contain colored water with a low pH. Estuaries constitute another type of body of water, consisting of arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and biological properties. Estuaries are the breeding grounds of much marine life, which makes the preservation of such systems an important aspect of water protection.

Wetlands are flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants. Wet flatlands are areas where mesophytic vegetation is more important than open water and which are commonly developed in filled lakes, glacial pits, and potholes, or in poorly drained coastal plains or flood plains. The term swamp is usually applied to a wetland where trees and shrubs are an important part of the vegetative association, and the term bog implies lack of solid foundation. Some bogs consist of a thick zone of vegetation floating on water.

Unique plant associations characterize wetlands in various climates and exhibit marked zonation characteristics around the edge in response to different thicknesses of the saturated zone above the firm base of soil material. Coastal marshes covered with vegetation adapted to saline water are common on all continents.

Some constructed reservoirs are similar to lakes, while others differ a great deal from them. Reservoirs with a large volume relative to their inflow and outflow are called storage reservoirs. Reservoirs with a large rate of into the reservoir and out of the reservoir (flow-through) compared to the reservoir volume are run-of-the-river reservoirs. The physical, chemical, and biological properties of water in the two types of reservoirs may vary appreciably. Also, water in storage reservoirs more closely resembles lake water, whereas water in run-of-the-river reservoirs is much like river water.

Impounding water in reservoirs may have some profound effects upon water quality, and these changes result from factors such as different velocities, changed detention time, and altered surface-to-volume ratios relative to the streams that were impounded. Some resulting beneficial changes due to impoundment are a decrease in the level of organic matter, a reduction in turbidity, and a decrease in hardness (calcium and magnesium content).

Some detrimental changes are lower oxygen levels due to decreased reaeration, decreased mixing, accumulation of pollutants, lack of a bottom scour produced by flowing water scrubbing a stream bottom, and increased growth of algae. Algal growth may be enhanced when suspended solids settle from impounded water, causing increased exposure of the algae to sunlight. Stagnant water in the bottom of a reservoir may be of low quality. Oxygen levels frequently go to almost zero near the bottom, and hydrogen sulfide is produced by the reduction of sulfur compounds in the low oxygen environment. Insoluble iron (Fe^{3+}) species are reduced to soluble iron (Fe^{2+}) species which must be removed prior to use of the water.

The unique temperature-density relationship of water results in the formation of distinct layers (stratification) within non-flowing bodies of water. During the summer, a surface layer (epilimnion) is heated by solar radiation and, because of its lower density, floats upon the bottom layer (hypolimnion). This phenomenon is called thermal stratification. When an appreciable temperature difference exists between the two layers, they do not mix but behave independently and have different chemical and biological properties. The epilimnion, which is exposed to light, may have a heavy growth of algae. As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic. In the hypolimnion, bacterial action on biodegradable organic material may cause the water to become anaerobic. As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.

The shear-plane, or layer between epilimnion and hypolimnion (the thermocline) and during the autumn, when the epilimnion cools, a point is reached at which the temperatures of the epilimnion and hypolimnion are equal. This disappearance of thermal stratification causes the entire body of water to behave as a hydrological unit, and the resultant mixing (the overturn) generally occurs in the spring. During the overturn, the chemical and physical characteristics of the body of water become much more uniform, and a number of chemical, physical, and biological changes may result. Biological activity may increase from the mixing of nutrients. Changes in water composition during overturn may cause disruption in water treatment processes (Cheremisinoff, 1995).

An increasing amount of attention has been given to thermal pollution, the raising of the temperature of a waterway by heat discharged from the cooling system or effluent wastes of an industrial installation. This rise in temperature may sufficiently upset the ecological balance of the waterway to pose a threat to the native life-forms. This problem has been especially noted in the vicinity of nuclear power plants. Thermal pollution may be combated by allowing wastewater to cool before emptying into the waterway which is often accomplished in large cooling towers.

The chemistry and biology of the oceans are unique because of the high salt content, depth, and other factors. The environmental problems of the oceans have increased greatly in recent years because of ocean dumping of pollutants, oil spills, and increased utilization of natural resources from the oceans. Moreover, many of the pollutants have a considerable lifetime in the ocean (Figure 4.3).

In many cases, oceans, rivers, and lakes have become polluted from discharges of liquid wastes from residential, commercial, and industrial sources, and many of these bodies of water have been reclaimed because of the construction of new wastewater treatment facilities. Both physical-chemical and biological processes are used to remove organic matter from the liquid wastewater stream. It is this organic matter that causes a depletion of oxygen *in rivers and lakes, with consequent anaerobic conditions leading to fish kills and noxious odors.*

The physical-chemical and biological processes remove an abundance of the organic matter, along with floatable scum and grease from the waste stream. Chemical disinfection inactivates bacteria, viruses, and protozoa in the waste stream. The physical and chemical processes used for removing solids from the waste stream include screening, sand and grit separation, chemical coagulation, and plain sedimentation. Biological processes include activated sludge, contact towers, and biological discs. The application of these treatment processes to residential, commercial, and industrial wastewaters has reduced the pollution load on many rivers, lakes, and harbors. There do remain, however, cases of large metropolitan areas that have not completed their cleanup campaigns, and in many other regions, discharges of untreated mixtures of sanitary wastes and storm waters occur during heavy rains.

These discharges emanate from large conduits that carry both sanitary and storm wastes. The impurities that run off the land during a storm mix with the sanitary wastes in the pipes, and the quantity of wastewater overtaxes the carrying capacity of the conduits. A portion of this mixture flows into the nearest body of water before it can reach the wastewater treatment facility. Where wastewater must be discharged into a lake or into a dry stream, a higher level of treatment must be employed, including removal of nutrients and colloidal matter.

See also: Aquasphere.

Water-Cooled Vibrating Grate Boiler

A water-cooled vibrating grate is a boiler grate made up of a tuyere grate surface mounted on a grid of water tubes interconnected with the boiler circulation system for positive cooling; the structure is supported by flexing plates allowing the grid and grate to move in a vibrating action; ash is automatically discharged.

The water-cooled vibrating grate (HVB) was developed for combustion of all types of biomass, peat, and refuse-derived fuels. It is preferred that the fuel have little or no mineral matter, i.e., low ash production.

The grate consists of two or four panel walls mounted on leaf springs. The panels are placed at an angle of 6° to the horizontal, and each panel is activated by a vibrating unit via a connecting rod. The panels are vibrated in pairs in counter-phase in order to balance external forces.

The fuel moves from the top of the grate to the lower end toward the slag hopper. The vibrating frequency is adjustable by means of a v-belt wheel. The start/stop sequence is controlled and can be freely adjusted to the condition of the fuel. Commonly used limits depend on the properties and condition of the fuel.

There are no mechanical joints or moving parts under the vibration grate that need lubrication. As it is thus only the strength of the construction materials that set the limit, the under-grate air can be preheated to 300°C (570°F) without any problems.

See also: Combustion, Combustors, Moving Grate Combustor.

Water Cycle

The water cycle describes the means by which water evaporates from the surface of the Earth, rises into the atmosphere, cools, condenses to form clouds, and falls again to the surface as precipitation. This system of the cycling of water is intimately linked with energy exchanges among the atmosphere, the ocean, and land that determine the climate of the Earth and cause much of natural climate variability. For example, approximately 75% of the energy (or heat) in the global atmosphere is transferred through the evaporation of water from the surface of the Earth. On land, water evaporates from the ground, mainly from soils, plants (through transpiration), lakes, and streams. In fact, approximately 15% of the water entering the atmosphere is from evaporation from the land surfaces and evapotranspiration from plants which (i) cools the surface of the Earth, (ii) cools the lower atmosphere, and (iii) provides water to the atmosphere to form clouds.

The major physical components of the global water cycle include (i) the evaporation from the ocean and land surfaces, (ii) the transport of water vapor by the atmosphere, precipitation onto the ocean and land surfaces, (iii) the net atmospheric transport of water from land areas to ocean, and (iv) the return flow of fresh water from the land back into the ocean. The additional components of oceanic water transport are few, including the mixing of fresh water through the oceanic boundary layer, transport by ocean currents, and sea ice processes.

Water Cycle

Water is practically everywhere on Earth. Moreover, it is the only known substance that can naturally exist in three phases as (i) a gas, (ii) a liquid, and (iii) a solid within the relatively small range of air temperatures and pressures found at the surface of the Earth. Water is essential for the existence of life on the Earth and acts as a conjunction between the major parts of the climate system of the Earth— air, clouds, the ocean, lakes, vegetation, snowpack, and glaciers.

Water vapor has a huge influence on the Earth insofar as water vapor is a powerful greenhouse gas, and it is a major driver of the weather and climate systems of the Earth; it travels around the globe, transporting latent heat – latent heat is heat obtained by water molecules as they transition from liquid or solid to vapor; the heat is released when the molecules condense from vapor back to liquid or solid form, creating cloud droplets and various forms of precipitation.

The water cycle is an illustration of the continuous movement of water within the Earth and atmosphere. The cycle is a complex system that includes many different processes. Liquid water evaporates into water vapor, condenses to form clouds, and precipitates back to Earth in the form of rain and snow. Water in different phases moves through the atmosphere (transportation). Liquid water flows across land (runoff), into the ground (infiltration and percolation), and through the ground (groundwater). Groundwater moves into plants (plant uptake) and evaporates from plants into the atmosphere (transpiration). Solid ice and snow can turn directly into gas (sublimation). The opposite can also take place when water vapor becomes solid (deposition).

One aspect of the water cycle – precipitation – is a vital component of how water moves through the water cycle, connecting the atmosphere, the ocean, and the land. Knowing where it rains, how much it rains, and the character of the falling rain, snow, or hail affords an understanding of the impact of precipitation on streams and rivers as well as surface runoff and groundwater.

The water cycle also illustrates the manner in which water evaporates from the surface of the Earth, rises into the atmosphere, cools and condenses into rain or snow in clouds, and falls again to the surface of the Earth as precipitation. The water falling on land collects in rivers and lakes, soil, and porous layers of rock, and much of it flows back into the oceans, where it will once more evaporate. The cycling of water in and out of the atmosphere is a significant aspect of the weather patterns of the Earth.

Moreover, the water cycle has no starting point, but, as a context for this text, the Sun, which drives the water cycle, heats the water in the oceans, and causes some of the water to evaporates (as vapor) into the air. Ice and snow can sublime directly (by omitting the liquid phase) into water vapor. Rising air currents take the vapor up into the atmosphere, along with water from evapotranspiration, which is water that is transpired from plants and evaporated from the soil. The vapor rises into the air where cooler temperatures cause the water vapor to condense into clouds.

Air currents move clouds around the globe; cloud particles collide, grow, and fall out of the sky as precipitation. Some of the precipitation falls as snow and can accumulate as ice caps and glaciers, which can store frozen water for thousands of years. The snowpack in warmer climates often thaw and melt when spring arrives, and the melted water flows overland as snowmelt.

Most of the precipitation falls back into the oceans or on to land, where, due to gravity, the precipitation flows over the ground as surface runoff. A portion of the runoff enters rivers in valleys in the landscape, with streamflow moving water toward the oceans. On the other hand, some of the runoff, and groundwater seepage, accumulate and are stored as freshwater in lakes, but not all of the runoff flows into rivers, though. Much of the runoff soaks into the ground (infiltration), some of which infiltrates deep into the ground and replenishes aquifers (saturated subsurface rock formation), which store considerable amounts of water for long periods of time. Some infiltration stays close to the land surface and can seep back into surface-water bodies (and the ocean) as groundwater discharge, and some groundwater finds openings in the land surface and emerges as freshwater springs.

Over time, the water continues to move – some to reenter the ocean, where the water cycle continues as outlined above.

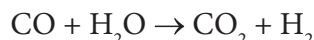
See also: Aquasphere, Biogeochemical Cycles, Hydrologic Cycle.

Water Gas

Water gas (carbureted blue gas) is a mixture of carbon monoxide and hydrogen formed by the action of air and then steam on hot coal or coke and enriched with hydrocarbon gases from the pyrolysis of oils.

On the other hand, semi-water gas is a mixture of water gas and producer gas that is made by passing a mixture of air and steam through heated coke. The heat generated when producer gas is formed keeps the temperature of the coke high enough to allow water gas to be formed.

The Lowe's water gas process is a process by which large amounts of hydrogen gas could be generated for residential and commercial use in heating and lighting. This gas provides a more efficient heating fuel than the common coal gas, or coke gas, which was used in municipal service. The process uses the water-gas shift reaction:

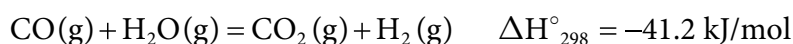


The process was discovered by passing high-pressure steam over hot coal, the major source of coke gas. Lowe's process improved upon the chimney systems by which the coal could remain superheated, thereby maintaining a consistently high supply of the gas. The reaction produced carbon dioxide and hydrogen, which, after a process of cooling and scrubbing, produced hydrogen gas.

See also: Gasification, Water-Gas Shift Reaction.

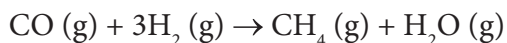
Water-Gas Shift Reaction

Even though the water-gas shift reaction is not classified as one of the principal gasification reactions, this reaction cannot be omitted in the analysis of chemical reaction systems that involve synthesis gas. Among all reactions involving synthesis gas, this reaction equilibrium is least sensitive to the temperature variation. In other words, its equilibrium constant is least strongly dependent upon the temperature. Therefore, this reaction equilibrium can be reversed in a variety of practical process conditions over a wide range of temperatures. Water-gas shift reaction in its forward direction is mildly exothermic as:



Even though all the participating chemical species are in forms of gas, scientists have not only believed that this reaction predominantly takes place at the heterogeneous surfaces of coal, but also that the reaction is catalyzed by carbon surfaces. Since the water-gas shift reaction is catalyzed by many heterogeneous surfaces and the reaction can also take place homogeneously as well as heterogeneously, a generalized understanding of water-gas shift reaction has been difficult to achieve. Even the kinetic rate information in the literature may not be immediately useful or applicable to a practical reactor situation.

Syngas product from a gasifier contains a variety of gaseous species other than carbon monoxide and hydrogen. Typically, they include carbon dioxide, methane, and water (steam). Depending upon the objective of the next processing scheme, the product composition of syngas may need to be preferentially readjusted. If the objective of the gasification were to obtain a high yield of methane, it would be preferred to have the molar ratio of hydrogen to carbon monoxide at 3:1, based on the following methanation reaction stoichiometry:



If the objective of generating syngas were in the synthesis of methanol via vapor-phase low-pressure process, the stoichiometrically consistent ratio between hydrogen and carbon monoxide would be 2:1. In these cases, the stoichiometrically consistent syngas mixture is often referred to as balanced gas, while a syngas composition that is substantially deviated from the principal reaction's stoichiometry is called "unbalanced gas."

If the objective of syngas production were to obtain a high yield of hydrogen, it would be advantageous to yield a higher ratio of H_2/CO by further converting CO (and H_2O) into H_2 (and CO_2) via water-gas shift reaction. However, if the final gaseous product is to be used in the fuel cell applications, carbon monoxide and carbon dioxide must be removed to acceptable levels by a process such as acid gas removal or other adsorption processes. In particular, for hydrogen PEM (proton exchange membrane) fuel cell operation, carbon monoxide must be thoroughly removed from the hydrogen gas.

Water-gas shift reaction is one of the major reactions in steam gasification process, where both water and carbon monoxide are present in ample amounts. Even though all four chemical species involved in the water-gas shift reaction are gaseous compounds at the reaction conditions of most gas processing, the water gas shift reaction, in the case of steam gasification of coal, predominantly takes place heterogeneously, i.e., on the coal solid surface. Water-gas shift reaction is catalyzed by a variety of metallic catalysts. The choice of specific kinds of catalysts has always been dependent upon the desired outcome, the prevailing temperature conditions, composition of gas mixture, and process economics. Many investigators have studied the water-gas shift reaction over a variety of catalysts including iron, copper, zinc, nickel, chromium, and molybdenum. Significant efforts have been spent in developing a robust catalyst system that has superior sulfur tolerance and wider applicable temperature range.

See also: Gasification, Synthesis Gas.

Water Pollutants

Water pollutants can be divided among some general classifications (Table W-5), and water pollution control is closely allied with the water supplies of communities and industries because both generally share the same water resources.

Table W-5 Examples of water pollutants and the effects.

Class of pollutant*	Effect
Acidity, alkalinity, salinity (in excess)	Water quality, aquatic life
Algal nutrients	Eutrophication
Asbestos	Human health
Biochemical oxygen demand	Water quality, oxygen levels
Chemical carcinogens	Incidence of cancer
Crude oil, products, and wastes	Effect of wildlife, health effects
Detergents	Eutrophication, wildlife, health effects
Inorganic pollutants	Toxicity, aquatic biota
Metal-organic combinations	Metal transport
Organic pollutants	Toxicity
Pathogens	Health effects
Pesticides	Toxicity, aquatic biota, wildlife
Polychlorinated biphenyls	Biological effects
Radionuclides	Toxicity
Sediments	Water quality, aquatic biota, wildlife
Sewage	Water quality, oxygen levels
Taste, odor, and color	Health effects, esthetics
Trace Elements	Health, aquatic biota

*Listed alphabetically

There is great similarity in the pipe systems that bring water to each home or business property, and the systems of sewers or drains that subsequently collect the wastewater and conduct it to a treatment facility. Treatment should prepare the flow for return to the environment so that the receiving watercourse will be suitable for beneficial uses such as general recreation, and safe for subsequent use by downstream communities or industries. In considering water pollution, it is useful to keep in mind an overall picture of possible pollutant cycles which involve the major routes of pollutant interchange among the biotic, terrestrial, atmospheric, and aquatic environments.

Water Pollution

Water pollution occurs when harmful substances – often chemicals or microorganisms – contaminate a stream, river, lake, ocean, aquifer, or other body of water, degrading water quality and rendering it toxic to humans or the environment. Thus, water pollution refers to any change in natural waters which may impair further use, caused by the introduction of organic or inorganic substances, or a change in temperature of the water.

Humans have also been polluting water since the early days of civilization. The development of towns and cities in close proximity to rivers also caused the rivers to become polluted by human waste and effluents. Indeed, whole civilizations have disappeared not only because of water shortages resulting from changes in the climate but also because of water-borne diseases, such as cholera and typhoid (Cartwright and Biddiss, 1972). In fact, one can wonder whether or not the castle moat actually protected the inmates from the attackers or whether the diseaseridden moat was fatal to both sides. Also, serious epidemics of water-borne diseases such as cholera, dysentery, and typhoid fever were caused by underground seepage from privy vaults into town wells (James and Thorpe, 1994). Such direct bacterial infections through water systems can be traced back for several centuries, even though the germ or bacterium as the cause of disease was not proved for nearly another century.

In terms of pollution of the oceans (also referred to as marine pollution), a considerable amount of the pollution originates on land – whether it occurs along the coast or inland – and is not always from ships at sea. Contaminants such as chemicals, nutrients, and heavy metals are carried from farms, factories, and cities by streams and rivers into bays and estuaries; from there, they travel out to sea.

See also: Pollutant, Pollution.

Water Removal from Gas Streams

Water is a common impurity in gas streams, and removal of water is necessary to prevent condensation of the water and the formation of ice or gas hydrates ($C_nH_{2n+2} \cdot xH_2O$). As an example from the area of renewable energy, the relative humidity of the gas stream inside the digester is 100%, so the gas is saturated with water vapors. To protect the energy conversion equipment from wear and from eventual damage, water must be removed from the produced the gas stream. The quantity of water contained by the gas stream depends on temperature. A part of the water vapor can be condensed by the cooling of the gas. This is frequently done in the gas pipelines transporting the gas stream from digester to a unit in which the water condensates on the walls of the sloping pipes and can be collected in a condensation separator, at the lowest point of the pipeline.

Water in the liquid phase causes corrosion problems in pipelines and equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas. The simplest method of water removal (refrigeration or cryogenic separation) is to cool the gas to a temperature at least equal to or (preferentially) below the dew point.

Most of the water associated with natural gas is removed by simple separation methods at or near the wellhead. However, the removal of the water vapor that exists in solution in natural gas requires a more complex treatment. This treatment consists of *dehydrating* the natural gas, which usually involves one of two processes: either absorption or adsorption.

A dehydration process is needed to eliminate water which may cause the formation of hydrates. Hydrates form when a gas or liquid containing free water experiences specific temperature/pressure conditions. Dehydration is the removal of this water from the produced natural gas and is accomplished by several methods. Among these is the use of ethylene glycol (glycol injection) systems as an absorption process. The process removes water and other

solids from the gas stream. Alternatively, adsorption dehydration may be used, utilizing dry-bed dehydrators towers, which contain desiccants such as silica gel and activated alumina, to perform the extraction.

In a majority of cases, cooling alone is insufficient and, for the most part, impractical for use in field operations. Other water removal processes use (i) hygroscopic liquids, such as diethylene glycol or triethylene glycol and (ii) solid adsorbents or desiccants, such as alumina, silica gel, and molecular sieves. Ethylene glycol can be directly injected into the gas stream in refrigeration plants.

The glycol has a chemical affinity for water and removes water from the gas stream. In this process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. Essentially, glycol dehydration involves using a glycol solution, usually either diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in a *contactor*. The glycol solution will absorb water from the wet gas, and once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The natural gas, having been stripped of most of its water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100°C, 212°F) and glycol (204°C, 400°F) makes it relatively easy to remove water from the glycol solution, allowing it to be reused in the dehydration process.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In the past, this methane was simply vented out of the boiler. In addition to losing a portion of the natural gas that was extracted, this venting contributes to air pollution and the greenhouse effect. In order to decrease the amount of methane and other compounds that are lost, flash tank separator-condensers work to remove these compounds before the glycol solution reaches the boiler. Essentially, a flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbons to vaporize (*flash*). The glycol solution then travels to the boiler, which may also be fitted with air or water-cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas (e.g., heavy hydrocarbon vapors, the *Drizo process*) or vacuum distillation are recommended.

Water may be removed from gas streams at the same time as hydrogen sulfide is removed. Moisture removal is necessary to prevent harm to anhydrous catalysts and to prevent the formation of hydrocarbon hydrates (e.g., $C_3H_8 \cdot 18H_2O$) at low temperatures. A widely used dehydration and desulfurization process is the glycolamine process, in which the treatment solution is a mixture of ethanolamine and a large amount of glycol. The mixture is circulated through an absorber and a reactivator in the same way as ethanolamine is circulated in the Girbotol process. The glycol absorbs moisture from the hydrocarbon gas passing up the absorber; the ethanolamine absorbs hydrogen sulfide and carbon dioxide. The treated gas leaves the top of the absorber; the spent ethanolamine-glycol mixture enters the reactivator tower, where heat drives off the absorbed acid gases and water.

Solid adsorbent or solid-desiccant dehydration is the primary form of dehydrating natural gas using adsorption, and usually consists of two or more adsorption towers, which are filled with a solid desiccant. Typical desiccants include activated alumina or a granular silica gel material. Wet natural gas is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower.

Solid-adsorbent dehydrators are typically more effective than glycol dehydrators, and are usually installed as a type of straddle system along natural gas pipelines. These types of dehydration systems are best suited for large volumes of gas under high pressure, and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To regenerate the desiccant, a high-temperature heater is used to heat gas to high temperature. Passing this heated gas through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further natural gas dehydration.

Silica gel (SiO_2) and alumina (Al_2O_3) have good capacities for water adsorption (up to 8% by weight). Bauxite (crude alumina, Al_2O_3) adsorbs up to 6% by weight water, and molecular sieves adsorb up to 15% by weight water. Silica is usually selected for dehydration of sour gas because of its high tolerance to hydrogen sulfide and to protect molecular sieve beds from plugging by sulfur.

In addition to separating any condensate from the wet gas stream, it is necessary to remove most of the associated water. Most of the liquid, free water associated with the extracted gas stream, is removed by simple separation methods; however, the removal of the water vapor that exists in solution in a gas stream requires a more complex treatment. This treatment consists of dehydrating the gas stream, which usually involves one of two processes: either absorption or adsorption.

Moisture may be removed from hydrocarbon gases at the same time as hydrogen sulfide is removed. Moisture removal is necessary to prevent harm to anhydrous catalysts and to prevent the formation of hydrocarbon hydrates (e.g., $C_3H_8 \cdot 18H_2O$) at low temperatures. A widely used dehydration and desulfurization process is the glycolamine process, in which the treatment solution is a mixture of ethanolamine and a large amount of glycol. The mixture is circulated through an absorber and a reactivator in the same way as ethanolamine is circulated in the Girbotol process. The glycol absorbs moisture from the hydrocarbon gas passing up the absorber; the ethanolamine absorbs hydrogen sulfide and carbon dioxide. The treated gas leaves the top of the absorber; the spent ethanolamine-glycol mixture enters the reactivator tower, where heat drives off the absorbed acid gases and water.

Absorption occurs when the water vapor is taken out by a dehydrating agent. Adsorption occurs when the water vapor is condensed and collected on the surface. In a majority of cases, cooling alone is insufficient and, for the most part, impractical for use in field operations. Other more convenient water removal options use (i) *hygroscopic* liquids (e.g., diethylene glycol or triethylene glycol) and (ii) solid adsorbents or desiccants (e.g., alumina, silica gel, and molecular sieves). Ethylene glycol can be directly injected into the gas stream in refrigeration plants.

Water Removal from Gas Streams – Absorption

An example of absorption dehydration is known as *glycol dehydration* – the principal agent in this process is diethylene glycol which has a chemical affinity for water. Glycol dehydration involves using a solution of a glycol such as diethylene glycol (DEG) or triethylene glycol (TEG), which is brought into contact with the wet gas stream in a *contactor*. In practice, absorption systems recover 90 to 99% by volume of methane that would otherwise be flared into the atmosphere.

In the process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. The glycol solution absorbs water from the wet gas, and, once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The dry gas stream is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the gas stream, is recycled through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100°C, 212°F) and glycol (204°C, 400°F) makes it relatively easy to remove water from the glycol solution.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In order to decrease the amount of methane and other compounds that would otherwise be lost, flash tank separator-condensers are employed to remove these compounds before the glycol solution reaches the boiler. The flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbon derivatives to vaporize (*flash*). The glycol solution then travels to the boiler, which may also be fitted with air- or water-cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or even before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas (e.g., heavy hydrocarbon vapors, the *Drizo process*) or vacuum distillation are recommended.

Another absorption process, the Rectisol process, is a physical acid gas removal process using an organic solvent (typically methanol) at subzero temperatures, and characteristic of physical acid gas removal processes, it can purify a gas stream down to 0.1 ppm v/v total sulfur, including hydrogen sulfide (H_2S) and carbonyl sulfide (COS), and carbon dioxide (CO_2) in the ppm v/v range. The process uses methanol as a wash solvent, and the wash unit operates under favorable temperatures below 0°C (32°F). To lower the temperature of the feed gas temperatures, it is cooled against the cold-product streams, before entering the absorber tower. At the absorber tower, carbon dioxide and hydrogen sulfide (with carbonyl sulfide) are removed. By use of an intermediate flash, co-absorbed products such as hydrogen and carbon monoxide are recovered, thus increasing the product recovery rate. To reduce the required

energy demand for the carbon dioxide compressor, the carbon dioxide product is recovered in two different pressure steps (medium pressure and lower pressure). The carbon dioxide product is essentially sulfur-free (hydrogen sulfide-free, carbonyl sulfide-free) and water-free. The carbon dioxide products can be used for enhanced oil recovery (EOR) and/or sequestration or as pure carbon dioxide for other processes.

See also: Absorption, Gas Cleaning.

Water Removal from Gas Streams – Adsorption

Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. It must be emphasized that *adsorption* differs from *absorption* in that absorption is not a physical-chemical surface phenomenon but a process in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). Dehydration using a solid adsorbent or solid-desiccant is the primary form of dehydrating the gas stream using adsorption, and usually consists of two or more adsorption towers, which are filled with a solid desiccant. Typical desiccants include activated alumina or a granular silica gel material. A wet gas stream is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower. There are several solid desiccants which possess the physical characteristic to adsorb water from the gas stream. These desiccants are generally used in dehydration systems consisting of two or more towers and associated regeneration equipment.

Molecular sieves – a class of aluminosilicates which produce the lowest water dew points and which can be used to simultaneously sweeten, dry gases and liquids – are commonly used in dehydrators ahead of plants designed to recover ethane and other higher-boiling hydrocarbon derivatives. These plants operate at very cold temperatures and require very dry feed gas to prevent formation of hydrates. Dehydration to -100°C (-148°F) dew point is possible with molecular sieves. Water dew points less than -100°C (-148°F) can be accomplished with special design and definitive operating parameters.

Molecular sieves are commonly used to selectively adsorb water and sulfur compounds from light hydrocarbon streams such as liquefied petroleum gas, propane, butane, pentane, light olefin derivatives, and alkylation feed. Sulfur compounds that can be removed are hydrogen sulfide, mercaptan derivatives, sulfide derivatives, and disulfide derivatives. In the process, the sulfur-containing feedstock is passed through a bed of sieves at ambient temperature. The operating pressure must be high enough to keep the feed in the liquid phase. The operation is cyclic in that the adsorption step is stopped at a predetermined time before sulfur breakthrough occurs. Sulfur and water are removed from the sieves by purging with fuel gas at 205 to 315°C (400 to 600°F).

Solid-adsorbent dehydrators are typically more effective than liquid absorption dehydrators (e.g., glycol dehydrators) and are usually installed as a type of straddle system along gas pipelines. These types of dehydration systems are best suited for large volumes of gas under very high pressure, and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To regenerate and recycle the desiccant, a high-temperature heater is used to heat gas to a very high temperature and passage of the heated gas stream through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further dehydration of the gas stream.

Although two-bed adsorbent treaters have become more common (while one bed is removing water from the gas, the other undergoes alternate heating and cooling), on occasion, a three-bed system is used: one bed adsorbs, one is being heated, and one is being cooled. An additional advantage of the three-bed system is the facile conversion of a two-bed system so that the third bed can be maintained or replaced, thereby ensuring continuity of the operations and reducing the risk of a costly plant shutdown.

Silica gel (SiO_2) and alumina (Al_2O_3) have good capacities for water adsorption (up to 8% by weight). Bauxite (crude alumina, Al_2O_3) adsorbs up to 6% by weight water, and molecular sieves adsorb up to 15% by weight water. Silica is usually selected for dehydration of sour gas because of its high tolerance to hydrogen sulfide and to protect molecular sieve beds from plugging by sulfur. Alumina *guard beds* serve as protectors by the act of attrition and may be referred to as an *attrition reactor* containing an *attrition catalyst* may be placed ahead of the molecular sieves to

remove the sulfur compounds. Downflow reactors are commonly used for adsorption processes, with an upward flow regeneration of the adsorbent and cooling using gas flow in the same direction as adsorption flow.

Solid desiccant units generally cost more to buy and operate than glycol units. Therefore, their use is typically limited to applications such as gases having a high hydrogen sulfide content, low dew point requirements, simultaneous control of water, and hydrocarbon dew points. In processes where cryogenic temperatures are encountered, solid desiccant dehydration is usually preferred over conventional methanol injection to prevent hydrate and ice formation.

See also: Adsorption, Gas Cleaning.

Water Removal from Gas Streams – Cryogenics

Another possibility for drying a gas stream is by cooling the gas in electrically powered gas coolers, at temperatures below 10°C (50°F), which allows a lot of humidity to be removed. In order to minimize the relative humidity, but not the absolute humidity, the gas can be warmed up again after cooling, in order to prevent condensation along the gas pipelines.

Thus, cryogenic upgrading makes use of the distinct boiling/sublimation points of the different gases particularly for the separation of carbon dioxide and methane. In the process, the raw (untreated) gas stream is cooled down to the temperatures where the carbon dioxide in the gas condenses or sublimates and can be separated as a liquid or a solid fraction, while methane accumulates in the gas phase. Water and siloxane derivatives are also removed during the cooling of the gas. However, the content of methane in the gas stream affects the characteristics of the gas, i.e., higher pressures and/or lower temperatures are needed to condense or sublime carbon dioxide when it is in a mixture with methane. Cooling usually takes place in several steps in order to remove the different gases in the gas stream individually and to optimize the energy recovery.

As an example, a hot gas stream containing water and carbon dioxide can be upgraded by cooling the gas to 40°C (104°F); most of the water is condensed. The remaining water is removed in the carbon dioxide removal step – the carbon dioxide to be removed from the gas stream to meet the specifications. The final concentration of carbon dioxide in the gas stream is determined by the specification of the Wobbe index. For carbon dioxide removal, considering the high partial pressure of carbon dioxide, both membranes and physical solvents can be chosen, where membranes are at their maximum scale and physical solvents are at their minimum scale (Alderton, 1993; Hall and Lokhandwala, 2004). The main advantage of the cryogenic process is that it is possible to obtain a gas stream with a high methane content of up to 99% v/v. The main disadvantage is that for the upgrading process, it is necessary to use many of technological equipment, especially compressors, turbines, and heat exchangers. This significant demand for additional equipment can make the cryogenic separation process extremely expensive.

See also: Gas Cleaning.

Water Removal from Gas Streams – Methanol-Based Processes

Methanol is probably one of the most versatile solvents in the natural gas processing industry. Historically, methanol was the first commercial organic physical solvent and has been used for dehydration, hydrate inhibition, gas sweetening, and liquids recovery. Most of these applications involve low temperature where the physical properties of methanol are advantageous compared with other solvents that exhibit high viscosity problems or even solids formation. Operation at low temperatures tends to suppress the most significant disadvantage of methanol – i.e., high solvent loss. Furthermore, methanol is relatively inexpensive and easy to produce, making the solvent an attractive alternate for gas processing applications.

The use of methanol has been further exploited in the development of the Rectisol process either alone or as toluene-methanol mixtures are used to more selectively remove hydrogen sulfide and move carbon dioxide to the overhead product. Toluene has an additional advantage insofar as carbonyl sulfide (carbonyl sulfide) is more soluble in toluene than in methanol. The Rectisol process was primarily developed to remove both carbon dioxide and hydrogen sulfide (along with other sulfur-containing species) from gas streams resulting from the partial oxidation

of coal, oil, and crude oil residua. The ability of methanol to absorb these unwanted components made it the natural solvent of choice. Unfortunately, at cold temperatures, methanol also has a high affinity for hydrocarbon constituents of the gas streams. For example, propane is more soluble in methanol than is carbon dioxide. There are two versions of the Rectisol process – the two-stage and the once-through. The first step of the two-stage process is desulfurization before shift conversion; the concentrations of hydrogen sulfide and carbon dioxide are approximately 1 and 5% v/v, respectively. Regeneration of the methanol following the desulfurization of the feed gas produces high sulfur feed for sulfur recovery. The once-through process is only applicable for high-pressure partial oxidation products. The once-through process is also applicable when the hydrogen sulfide to carbon dioxide content is unfavorable, in the neighborhood of 1:50.

Recently, a process using methanol has been developed in which there is the simultaneous capability to dehydrate, to remove acid gas, and to control hydrocarbon dew point (Rojey and Larue, 1988; Rojey *et al.*, 1990). The IFPEXOL-1 is used for water removal and hydrocarbon dew point control; the IFPEXOL-2 process is used for acid gas removal. The novel concept behind the IFPEXOL-1 process is to use a portion of the water-saturated inlet feed to recover the methanol from the aqueous portion of the low-temperature separator. That approach has solved a major problem with methanol injection in large facilities, the methanol recovery via distillation. Beyond that very simple discovery, the cold section of the process is remarkably similar to a basic methanol injection process. Modifications to the process include water washing the hydrocarbon liquid from the low temperature separator to enhance the methanol recovery. The IFPEXOL-2 process for acid gas removal is very similar to an amine type process except for the operating temperatures. The absorber operates below -20°F to minimize methanol losses, and the regenerator operates at approximately 90 psi. Cooling is required on the regenerator condenser to recover the methanol. This process usually follows the IFPEXOL-1 process, so excessive hydrocarbon absorption is not as great a problem.

See also: Gas Cleaning.

Water System

A water system comprises a drainage basin and its physical, chemical, and biological constituents, including water networks, ecosystems, the built environment, the oceanic and atmospheric systems that govern evaporation and precipitation in the basin, and the source water bodies and terminal lakes or seas into which the water flows. In whichever system water is located, water is a complex system of chemical species that has received considerable study (Eglington, 1975; Jenne, 1979; Melchior and Bassett, 1990). Indeed, the public has been introduced to the issues of water pollution for the past several years, not the least of which is the pollution of Boston Harbor by tea being imported from England which played a significant role in the formation of the United States (Easterbrook, 1995).

Briefly, when rain falls and seeps deep into the earth, filling the cracks, crevices, and porous spaces of an aquifer (basically an underground storehouse of water), it becomes groundwater which is one of the least visible but most important natural resources. Many towns and villages rely upon groundwater – pumped to the surface of the Earth – for drinking water. For some people in rural areas, it is the only freshwater source. Groundwater gets polluted when contaminants—from pesticides and fertilizers to waste leached from landfills and septic systems—make their way into an aquifer, rendering it unsafe for human use. Ridding groundwater of contaminants can vary from difficult to impossible. Once polluted, an aquifer may be unusable for decades, or even thousands of years. Groundwater can also spread contamination far from the original polluting source as it seeps into streams, lakes, and oceans.

On the other hand, surface water covers approximately 70% of the surface of the earth in the form of oceans, lakes, rivers, and streams. In terms of non-oceanic water, surface water from freshwater sources is in danger from various pollutants (Jazib, 2018). In fact, pollution by nutrients, which includes nitrates and phosphates, is the leading type of contamination in the freshwater sources. While plants and animals need these nutrients to grow, they have become a major type of pollutant due to the runoff of farm waste and fertilizer. Municipal and industrial waste discharges into fresh water sources also contribute toxins along with the waste from domestic sources and also from industrial sources, although many countries have laws in place to cease such discharges.

Thus, pollution of a water system occurs when harmful substances – such as chemicals or microorganisms – contaminate a water system (stream, river, lake, ocean, aquifer, or other body of water) causing degrading water quality and rendering the water toxic only to humans but also to other floral and faunal life forms. In fact, water is

uniquely vulnerable to pollution because it can dissolve more substances than any other liquid on the Earth. Toxic substances from farms, towns, and factories readily dissolve into and mix with water leading to water pollution.

See also: Aquasphere.

Water Washing

Water washing, in terms of the outcome, is analogous to washing with potassium carbonate for gas cleaning, and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical, and there is also a relatively high absorption of hydrocarbons, which are liberated at the same time as the acid gases.

See also: Gas Cleaning.

Wave Energy

Tidal energy (tidal power) has the advantage of being completely predictable: The tides occur with perfect regularity every day. In contrast, waves vary in strength, from a mere ripple to large storm waves. Yet sites with deep, concentrated tidal currents are not common, and waves wash all shores.

Wave energy is the transport of energy by ocean surface waves. Waves are generated by wind passing over the surface of the sea. As long as the waves propagate slower than the wind speed just above the waves, there is an energy transfer from the wind to the waves. Both air pressure differences between the upwind and the lee side of a wave crest, as well as friction on the water surface by the wind, making the water to go into the shear stress, cause the growth of the waves.

Thus, waves are formed due to exchange of power from wind to the water. The winds are formed due to the Sun. The land and water operate as cosmological discharge hoarders; deep sea water is the result of resourcefulness of these. When the water is hot, it is heated and it turns into a form of steam which further turns into air above it. The hot air then ascends and displaces cold air, which falls down to be heated by the water in turn. As a result, air currents are produced. As these currents propel on the surface of the water, the roughness between them causes the water to extend, the result of which is miniature currents. This affects the surface to contact between the water and wind to extend, and gradually larger waves. In addition, waves can also be generated by huge disturbances, which result in tsunamis. Despite the fact that they are uncommon, it is still significant while shaping utmost load energy tool must survive.

Wave height is determined by wind speed, the duration of time the wind has been blowing, fetch (the distance over which the wind excites the waves), and by the depth and topography of the seafloor (which can focus or disperse the energy of the waves). A given wind speed has a matching practical limit over which time or distance will not produce larger waves. In general, larger waves are more powerful, but wave power is also determined by wave speed, wavelength, and water density.

As an alternative energy, wave energy is the capture of the energy of waves for a useful purpose, such as electricity generation, water desalination, or the pumping of water (into reservoirs). Wave power is used synonymously with wave energy, or references the generation of electricity from the energy of waves. As with tidal power, wave power may be considered a form of hydropower whereby the definition of hydropower is expanded to encompass any type of energy gained from the movement of water.

There are at least six different technologies for harvesting wave power which are (i) the attenuator, (ii) the point absorber, (iii) the oscillating wave surge converter, (iv) the oscillating water column, (v) the overtopping device, and (v) the submerged pressure differential.

The attenuator: Long, tubelike floats linked end-to-end by flexible hoses rock as waves pass under them. The motion pressurizes oil, which drives generators. The world's first commercial wave-power farm, along the coast of Portugal, uses this technology and was being installed as of mid-2008. The point absorber is a device in which a float bobs up down on the surface of the waves and a vertical shaft is worked by the motion, pressurizing generators. The oscillating wave surge converter is a device in which a buoy-like arm is tethered to the bottom and waved back and forth like an upside-down pendulum as waves surge past. In the oscillating water column device, a sealed column

with water in its lower portion and air in its upper portion is connected to the sea. Wave action causes the water part of the column to rise and fall, raising and lowering the air and causing air-driven turbines to rotate. The overtopping device allows waves to slosh over the top of a barrier, and the water flows back to the sea through a turbine. The submerged pressure differential uses a drum or tube along which a piston moves is anchored to the ocean floor not far below the surface. Water pressure on the piston varies as waves pass above, causing it to move back and forth in the shaft.

It is approximated that the entire power of waves broke on the seashore is approximately 2-3 terawatts. The best possible locations for wave energy having density typically 65 MW solitary mile of seashore, or 70 kW of power for every meter of wave peak length. In winters, this number raises up to 170 kW/m and can attain as high as 1 MW/m during storms. In winter, waves possess more energy than in other seasons. It is essential to notice that once a wave is produced, it could voyage greater distances without any loss in energy. This provides waves a total of certainty: yet in phase of modest wind and hence miniature wave produced. Waves generated from distant areas can still be added to energy generation.

See also: Ocean Energy, Tidal Energy.

Weibull Distribution

The speed of the wind is highly variable, and in order to be able to predict the production of a wind turbine, it is necessary to know exactly how often the wind blows strongly. Typically, the wind is measured with an anemometer and the mean wind speed is recorded every 10 minutes, and the resulting data can be sorted into wind speed classes of 1 m/s each. The energy contained in the wind at a certain site may then be expressed by this frequency distribution.

In addition, the Weibull distribution is often a good approximation for the wind speed distribution:

$$f(v) = \frac{k}{A} \left(\frac{v}{A} \right)^{k-1} \exp \left(- \left(\frac{v}{A} \right)^k \right)$$

In this equation, A is the Weibull scale parameter in m/s which is a measure for the characteristic wind speed of the distribution. A is proportional to the mean wind speed. k is the Weibull form parameter which specifies the shape of a Weibull distribution and takes on a value of between 1 and 3. A small value for k signifies very variable winds, while constant winds are characterized by a larger value k.

Thus, the Weibull distribution is often a good approximation for the wind speed distribution. Weibull Analysis is an effective method of determining reliability characteristics and trends using a relatively small sample size of field.

See also: Wind Speed and Wind Gusts.

Wellman-Galusha Process

The Wellman-Galusha process has been in commercial use for more than 50 years, and there are two types of gasifiers, which are (i) the standard type of gasifier and (ii) the agitated type of gasifier which can have a rated capacity of an agitated unit may be 25% (or more) higher than that of a standard gasifier of the same size.

The gasifier is water-jacketed and, therefore, the inner wall of the vessel does not require a refractory lining. Agitated units include a varying speed revolving horizontal arm which also spirals vertically below the surface of the coal bed to minimize channeling and to provide a uniform bed for gasification. A rotating grate is located at the bottom of the gasifier to remove the ash from the bed uniformly. Steam and oxygen are injected at the bottom of the bed through tuyeres. Crushed coal is fed to the gasifier through a lock hopper and vertical feed pipes. The fuel valves are operated so as to maintain a relatively constant flow of coal to the gasifier to assist in maintaining the stability of the bed and, therefore, the quality of the product gas.

These are two types of gasifiers, the standard type and the agitated type, and the rated capacity of an agitated unit may be 25% (or more) higher than that of a standard gasifier of the same size. An agitated gasifier is capable of treating volatile caking bituminous coals.

The gasifier is water-jacketed and, therefore, the inner wall of the vessel does not require a refractory lining. Agitated units include a varying speed revolving horizontal arm which also spirals vertically below the surface of the coal bed to minimize channeling and to provide a uniform bed for gasification. A rotating grate is located at the bottom of the gasifier to remove the ash from the bed uniformly. Steam and oxygen are injected at the bottom of the bed through tuyeres.

Crushed coal is fed to the gasifier through a lock hopper and vertical feed pipes. The fuel valves are operated so as to maintain a relatively constant flow of coal to the gasifier to assist in maintaining the stability of the bed and, therefore, the quality of the product gas. The air or oxygen which is injected into the gasifier passes over the top of the water jacket and thereby picks up the steam required for the process. The air-steam mix is introduced into the ash bin section underneath the grate and is then distributed through the grate into the bed, and passes upward through the ash, combustion, and gasification zones. The product gas contains primarily carbon monoxide, carbon dioxide, hydrogen, and nitrogen (if air is injected) which, being hot, dries and preheats the incoming coal before leaving the gasifier.

The product gas is passed through a cyclone, in which fine ash and char particles are removed, and if the sulfur content of the gas is acceptable, it may be used directly. If the sulfur content of the gas is too high, the gas can be scrubbed and cooled in a direct-contact countercurrent water cooler and then treated for sulfur removal. Use of air to support combustion will yield a low heat content gas, but use of oxygen will yield a medium heat-content gas.

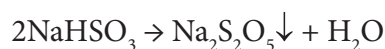
See also: Gasification.

Wellman-Lord Process

The Wellman-Lord Process is a regenerable process to remove sulfur dioxide from gas streams without creating a throwaway sludge product. The process reduces stack gas sulfur dioxide concentration to less than 250 ppm v/v and can achieve approximately 99.9% sulfur recovery.

The *Wellman-Lord process* (Figure 312) is a versatile process that relies on the reaction of sulfur dioxide with sodium sulfate to produce sodium bisulfite. The bisulfite solution is next heated in an evaporator, which reverses the reaction, liberating a concentrated stream of sulfur dioxide. The sulfur dioxide can then be converted to either elemental sulfur or sulfuric acid.

After lowering the temperature the bisulfite is converted to the sodium pyrosulfite which has a low solubility and precipitates. Heating reverses the two previously described chemical reactions, and the sodium pyrosulfite is converted to sulfur dioxide and sodium sulfite. The sulfur dioxide can be used for further reactions, and the sulfite is reintroduced into the process.



The process can be divided into two main stages. The first stage is an absorption stage in which the hot flue gases are passed through a pre-scrubber where ash, hydrogen chloride, hydrogen fluoride, and sulfur trioxide (SO_3) are removed. The gases are then cooled and fed into the absorption tower. A saturated solution of sodium sulfite is then sprayed into the top of the absorber onto the flue gases; the sodium sulfite reacts with the sulfur dioxide

forming sodium bisulfite. The concentrated bisulfate solution is collected and passed to an evaporation system for regeneration.

The second stage is a regeneration stage in which the sodium bisulfite is broken down, using steam, to release the sodium sulfite, which is recycled back to the flue gases. The remaining product (the released sulfur dioxide) is converted to elemental sulfur, sulfuric acid, or liquid sulfur dioxide. This system offers a number of advantages over alternative systems, the main one being that the sorbent is regenerated during the combustion process and is continuously recycled.

Initially, the process was based on potassium sulfite, but the economic prognosis was poor and the later version used sodium sulfite. Because of side reactions forming thiosulfate (nonregenerable), there is a small makeup requirement in the form of trona (sodium carbonate).

See also: Gasification.

Wet Air Oxidation

The wet air oxidation process is the oxidation (using air) of dissolved or suspended components in water using oxygen as the oxidizer. The process was developed for destruction of organic contaminants, and, in this process, wastewater is exposed to air under elevated temperature and pressure, thus causing organic compounds to oxidize completely or at least decomposing them into forms that are more easily treated.

In the process, oxidation reactions occur in superheated water at a temperature above the boiling point of water (100°C, 212°F), but below the critical point (374°C, 705°F). The system must be maintained under pressure to avoid excessive evaporation of water. The process is predominately used for treating wastewater (Zimpro process).

Commercial systems typically use a bubble column reactor, where air is bubbled through a vertical column that is liquid full of the hot and pressurized wastewater. Fresh wastewater enters the bottom of the column, and oxidized wastewater exits the top. The heat released during the oxidation is used to maintain the operating temperature. The majority of commercial wet oxidation systems are used to treat industrial wastewaters, such as those containing dissolved sulfides. In particular, the process can be used to increase the biodegradable properties of compounds that are normally refractory (resistant) to biological oxidation.

Wet Gas

A wet gas (or a wet gas stream) is any gas with a small amount of liquid present (not necessarily water but often as higher-boiling hydrocarbon derivatives). In fact, the term wet gas has been used to describe a range of conditions varying from a humid gas which is gas saturated with liquid vapor to a multiphase flow system with a 90% volume of gas. Wet gas is a particularly important concept in the field of flow measurement, as the varying densities of the constituent material present a significant problem. Although the example used here is natural gas, the same rationale is also applied to gas streams produced from alternate energy sources such as biomass and waste.

Using natural gas as the example, wet gas has the same basic composition as dry natural gas, though with additional components. Wet gas contains approximately 85% v/v methane and other constituents such as ethane, propane, butane, and, in some instances hydrocarbon derivative up to and including octane. It is the higher-boiling hydrocarbon constituents that make the gas wet. On the other hand, dry gas is gas that is almost completely methane, with a higher methane content making the gas drier. Dry gas is often found in areas without wet gas but can come from similar regions.

Again, using natural gas as an example of wet gas flows are in the production of natural gas from a formation through. Natural gas is a mixture of hydrocarbon derivatives with quantities of various non-hydrocarbon compounds which exists in either the gaseous phase or the liquid phase or in solution with crude oil in porous rock formations (reservoirs). The amount of hydrocarbon derivatives present in the liquid phase of the wet gas extracted for the reservoir depends on the reservoir temperature and pressure conditions, which change over time as the gas and liquid are removed.

Changes in the liquid and gas content also occur when a wet gas is transported from a reservoir at high temperature and pressure to the surface where it experiences a lower temperature and pressure. The presence and changeability of this wet gas can cause problems and errors in the ability to accurately measure the gas phase flowrate. It is necessary to be able to measure these wet gas flows accurately to quantify production from individual wells and to maximize the use of equipment and resources which will assist with the reduction of costs.

See also: Crude Oil, Gas Condensate, Natural Gas.

Wet Milling Process

The corn wet milling process separates corn into its four basic components: starch, germ, fiber, and protein. There are several basic steps to accomplish this process.

1. First, the incoming corn is visually inspected and cleaned. Refinery people inspect arriving corn shipments and clean them two or three times to remove cob, dust, chaff, and any other foreign materials before the next processing stage, steeping. Effective screening process can save a great deal of trouble in the subsequent stages.
2. Second, it is steeped to initiate bond breaking of starch and protein. Steeping is typically carried out in stainless steel tanks. Each steep tank (or steeping tank) holds approximately 3,000 bushels of corn soaked in water at 50 °C for 30-40 hours. During steeping, the kernels absorb water, thereby increasing their moisture levels from 15% to 45% by weight and also more than doubling in size. The addition of 0.1 % sulfur dioxide (SO₂) to the water suppresses excessive bacterial growth in the warm environment. As the corn swells and softens, the mild acidity of the steeping water begins to loosen the gluten bonds within the corn and eventually release the starch. A bushel is a unit of volume measure used as a dry measure of grains and produce. A bushel of corn or milo weighs 56 pounds, a bushel of wheat or soybeans weighs 60 pounds, and a bushel of sunflowers weighs 25 pounds.
3. Third, it involves a coarse grind to separate the germ from the rest of the kernel. Germ is the embryo of a kernel of grain. This is accomplished in cyclone separators, which spin the low-density corn germ out of the slurry. Therefore, this cyclone separator is called a germ separator. The germs, which contain approximately 85% of corn's oil, are pumped onto screens and washed repeatedly to remove any starch left in the mixture. A combination of mechanical and solvent processes extracts the oil from the germ. The oil is then refined and filtered into finished corn oil. The germ residue is saved as another useful component of animal feeds. Both corn oil and germ residue are important by-products of this process.
4. As the fourth step, the remaining slurry, consisting of fiber, starch, and protein, is finely ground and screened to separate the fiber from the starch and protein. After the germ separation step described in (3), corn and water slurry goes through a more thorough grinding in an impact or attrition-impact mill to release the starch and gluten from the fiber in the kernel. The suspension of starch, gluten, and fiber flows over fixed concave screens, which catch fiber but allow starch and gluten to pass through. The fiber is collected, slurried, and screened again to reclaim any residual starch or protein, then piped or sent to the feed house as a major ingredient of animal feeds. The starch-gluten suspension, called mill starch, is piped or sent to the starch separators.
5. Starch is separated from the remaining slurry in hydrocyclones. By centrifuging mill starch, the gluten is readily spun out due to the density difference between starch and gluten. Starch is denser than gluten. Separated gluten can be used for animal feeds. The starch, with just 1-2% protein remaining, is diluted, washed 8 to 14 times, re-diluted, and re-washed in hydrocyclones to remove the last trace of protein and produce high-quality starch, typically more than 99.5% pure. Some of the starch is dried and marketed as unmodified cornstarch; some other portion is modified into specialty starches, but most is converted into corn syrups and dextrose. Cornstarch has a variety of industrial and domestic uses. All these are important by-products of the process that make the corn distillers' profitability improve.

6. Sixth, the cornstarch then is converted to syrup, and this stage is called starch conversion step. Starch-water suspension is liquefied in the presence of acid and/or enzymes. Enzymes help convert the starch to dextrose that is soluble in water as an aqueous solution. Treatment with another enzyme is usually carried out, depending upon the desired process outcome. The process of acid and enzyme reactions can be stopped or terminated anytime throughout the process to produce a right mixture of sugars like dextrose and maltose for syrups to meet desired specifications. For example, in some cases, the conversion of starch to sugars can be halted at an early stage to produce low-to-medium sweetness syrups. In other cases, however, the starch conversion process is allowed to proceed until the syrup becomes nearly all dextrose. After this conversion process, the syrup is then refined in filters, centrifuges, or ion-exchange columns, and excess water is evaporated to result in concentrated syrup. Syrup can be sold directly as is, crystallized into pure dextrose, or processed further to produce high-fructose corn syrup.
7. Seventh, syrups can be made into several other products through a fermentation process. Dextrose is one of the most fermentable forms of all of the sugars. Dextrose is also called corn sugar and grape sugar, and dextrose is a naturally occurring form of glucose. Dextrose is better known today as glucose. Following the conversion of starch to dextrose, corn refiners pipe and send dextrose to fermentation units/facilities where dextrose is converted to ethanol by traditional yeast fermentation. Using a continuous process, the fermenting mash is allowed to flow, or cascade, through several fermenters in series until the mash is fully fermented and then leaves the final tank. In a batch fermentation process, the mash stays in one fermenter for approximately 48 hours before the distillation process is initiated. Generally speaking, a continuous mode is more effective with a higher fermenter throughput, whereas a higher-quality product may be obtained from a batch mode.
8. As the eighth step, ethanol separation follows the fermentation step. The resulting broth is distilled to recover ethanol or concentrated through membrane separation to produce other by-products. Carbon dioxide generated from fermentation is recaptured for sale, and the nutrients still remaining in the broth after fermentation are used as components of animal feed ingredients. These by-products also help the overall economics of the corn refineries.

Even though the term by-product was used throughout the process description; co-product may be a better term, since these products are not only valuable but also targeted in the master plan of corn distillers.

See also: Corn-to-Ethanol Process.

Wet Oxidation Processes

The wet oxidation processes are based on reduction-oxidation (Redox) chemistry to oxidize the hydrogen sulfide to elemental sulfur in an alkaline solution containing an oxygen carrier. Vanadium and iron are the two oxygen carriers that are used.

The best example of a process using the vanadium carrier is the Stretford process. The most prominent examples of the processes using iron as a carrier are the LO-CAT process and the SulFerox process. The Stretford process using vanadium finds little use now because of the toxic nature of the vanadium solution, and iron-based processes are more common.

Both the LO-CAT process and the SulFerox process are essentially the same in principle. The SulFerox process differs from the LO-CAT in that the oxidation and the regeneration steps are carried out in separate vessels and sulfur is recovered from the filters, melted, and sent to sulfur storage. Also, the SulFerox process uses a higher concentration of iron chelates (approximately 2 to 4% by weight vs. 0.025 to 0.3% by weight for the LO-CAT process). Both processes are capable of up to 99+% sulfur recovery. However, using the processes for Claus tail gas treating requires hydrolysis of all the sulfur dioxide in the tail gas to hydrogen sulfide because the sulfur dioxide will react with the buffering base potassium hydroxide (KOH) and form potassium sulfate (K₂SO₄) which will consume the buffering solution and quickly saturate it.

Wet Scrubbers

Wet scrubbers are devices that utilize gas-liquid contacting to cool the gas stream, condense high-boiling hydrocarbons, dissolve some constituents, and separate particles from gas streams.

There is a large variety of wet scrubbers; however, all have one of three basic operations: (i) gas-humidification – the gas-humidification process conditions fine particles to increase their size so they can be collected more easily, (ii) gas-liquid contact – one of the most important factors affecting collection efficiency, and (iii) gas-liquid separation – regardless of the contact mechanism used, as much liquid and dust as possible must be removed and when contact is made, dust particulates and water droplets combine to form agglomerates – as the agglomerates grow larger, they settle into a collector.

The cleaned gases are normally passed through a mist eliminator (demister pads) to remove water droplets from the gas stream. The dirty water from the scrubber system is either cleaned and discharged or recycled to the scrubber. Dust is removed from the scrubber in a clarification unit or a drag chain tank. In both systems, solid material settles on the bottom of the tank. A drag chain system removes the sludge and deposits it into a dumpster or stockpile.

Wet scrubbers (spray-tower scrubbers) are categorized by pressure drop as follows: (i) low-energy scrubbers, (ii) low-to-medium-energy scrubbers, (iii) medium-to-high-energy scrubbers, and (iv) high-energy scrubbers. In the simple, gravity-spray-tower scrubber, liquid droplets formed by liquid atomized in spray nozzles fall through rising exhaust gases and dirty water is drained at the bottom.

A type of wet scrubber that has been widely applied to coal gas is the venturi scrubber; gas streams are passed through a tube to contact with water, which is added at the throat. The throat promotes intimate mixing of the gas and liquid, which forms droplets ranging in size from 100 to 1,000 microns, and collects particulates mainly by inertial impaction.

Other wet scrubber designs that might be applied to coal gas are plate scrubbers (sieves, bubble caps, and impingement plates), massive packing (rings, saddles), fibrous packing (plastic, spun glass, fiber glass, and steel wool), centrifugal (cyclone), and directional baffles (louvres, zigzags, disk, and donut).

Wet Scrubbing Systems

Wet scrubbing systems, particularly amine or potassium carbonate systems, are used for the removal of acid gases such as hydrogen sulfide or carbon dioxide. Most systems depend on chemical reaction and can be designed for a wide range of pressures and capacities. They were once widely used to remove carbon dioxide in steam reforming plants, but have generally been replaced by pressure swing adsorption units except where carbon monoxide is to be recovered. Wet scrubbing is still used to remove hydrogen sulfide and carbon dioxide in partial oxidation plants.

Wet scrubbing systems remove only acid gases or heavy hydrocarbons, but they do not remove methane or other hydrocarbon gases; hence, they have little influence on product purity. Therefore, wet scrubbing systems are most often used as a pretreatment step, or where a hydrogen-rich stream is to be desulfurized for use as fuel gas.

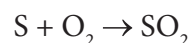
Wet Sulfuric Acid Process

The wet sulfuric acid process (WSA process) is one out of several desulfurization processes which, since its introduction in the 1980s, has been recognized as an efficient process for recovering sulfur from various process gasses in the form of commercial-quality sulfuric acid (H_2SO_4).

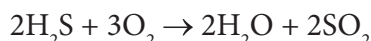
Wet catalysis processes differ from other contact sulfuric acid processes in that the feed gas still contains moisture when it comes into contact with the catalyst. The sulfur trioxide formed by catalytic oxidation of the sulfur dioxide reacts instantly with the moisture to produce sulfuric acid in the vapor phase to an extent determined by the temperature. Liquid acid is subsequently formed by condensation of the sulfuric acid vapor and not by absorption of the sulfur trioxide in concentrated sulfuric acid, as is the case in contact processes based on dry gases. The concentration of the product acid depends on the $\text{H}_2\text{O}/\text{SO}_3$ ratio in the catalytically converted gases and on the condensation temperature.

The wet catalysis process is especially suitable for processing the wet gasses obtained by the combustion of hydrogen sulfide (H_2S) containing off-gasses. The combustion gasses are merely cooled to the converter inlet temperature of approximately 420 to 440°C (790 to 825°F). To process these wet gases in a conventional cold-gas contact process (DCDA) plant would necessitate cooling the gas to an economically unacceptable extent to remove the large excess of moisture.

The chemistry of the process involves several steps. In the first step, sulfur is burned to produce sulfur dioxide:



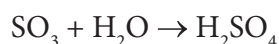
Hydrogen sulfide is incinerated to sulfur dioxide:



Sulfur dioxide is then oxidized to sulfur trioxide using oxygen in the presence of a vanadium (V) oxide catalyst:



The sulfur trioxide is hydrated and converted to sulfuric acid (H_2SO_4):



The last step is the condensation of the sulfuric acid to liquid 97-98% sulfuric acid.

Wheat Straw

Wheat is harvested across the United States, and its straw is an ideal agricultural residue for use in paper and paper products. The lignin content is comparable to hardwoods, and it has one of the highest cellulose contents of all of the agricultural fibers. When farmed intensively, wheat straw can be produced at a rate of 50 bushels/acre, yielding 1-3 tons per acre (depending on whether it is dry land or irrigated).

Wheat straw is clearly the most abundant non-wood plant material available for pulp and papermaking in the United States. The amount of wheat straw available for pulp production varies depending on the type of wheat grown, the harvest efficiency, and the amount that must be left on the field to comply with any residue management provisions and regulations.

Straw papers are known to possess good printing qualities and are made from pulp requiring low energy relative to that required to process wood pulp. Technicians have found that wheat straw must be pulped under conditions of less energy and fewer chemicals than wood pulps to maximize pulp yields. To make the strongest product, paper-makers will likely combine some stronger hardwood, kenaf, or hemp pulp with straw pulp.

Wheat straw is one of the major agricultural by-products that is currently not used as industrial raw material on a significant scale except for only a minor portion that is reserved as animal feed, household fuel, or as raw materials for paper industry.

See also: Biomass, Straw.

Willow

Willow has several characteristics that make it ideal for woody crop systems, including high yields, ease of propagation, a broad genetic base, a short breeding cycle, and the ability to resprout after multiple harvests. A sustainable system has been devised for willow biomass production by planting unrooted stem cuttings at a density of 4,000-8,000 plants per acre. Willow can achieve high yields, typically reaching 15-25 feet in height in three years, at which

time they can be harvested using modified agricultural equipment that cuts and chips the biomass in one operation. They resprout vigorously from their stumps (coppice) following harvest, with 7 to 8 harvesting cycles possible from an initial planting.

See also: Biomass, Wood.

Wind Energy

Wind energy is the form of energy created by wind which is the flow of air on a large scale that is caused by differences in atmospheric pressure. When a difference in atmospheric pressure exists, air moves from the higher to the lower pressure area, resulting in winds of various speeds. Globally, the two major driving factors of large-scale wind patterns (the atmospheric circulation) are the differential heating between the equator and the poles (difference in absorption of solar energy leading to buoyancy forces) and the rotation of the Earth.

In terms of alternative energy, the term wind energy refers to the energy that is harnessed from wind for practical purposes. The term wind power is used synonymously as the conversion of wind energy into a useful form of energy, or more specifically as the generation of electricity from the wind. Among ways in which wind energy can be harnessed are wind turbines to make electrical power, windmills for mechanical power, windpumps for water pumping or drainage, or sails to propel ships.

The energy from the sun does not strike Earth evenly, and, hence, it is to be expected that the predictability of wind current is minimized. The air around the equator absorbs more energy than the air above the poles. This difference causes air, a fluid much like water, to move in currents. Air, like any substance, expands when it is warmed and contracts when it is cooled. Warm air, because it is less dense than cool air, is lighter, so it rises, much like a less-dense piece of wood rises to the top of more-dense water. This effect can be seen by looking at the hot air above a fire, which seems to shimmer as it expands and moves upward, carrying smoke and ash with it. Cold air, because it shrinks, is denser than surrounding warm air, so it sinks. This property explains in part why a freezer generally operates more efficiently when it is placed at the bottom of a refrigerator rather than at the top and why the basement is generally colder than the upper levels of a house.

As warm air rises, colder, heavier air flows in to replace it, causing a current of air, i.e., wind. The rotation of the Earth also plays a role in wind production. If the Earth did not rotate, air heated at the equator would rise only approximately 6 miles (10 kilometers) into the atmosphere and flow toward the North Pole and the South Pole, where it would cool, sink, and return to the equator. Earth's rotation allows winds to circulate in more or less predictable patterns across the Northern Hemisphere and Southern Hemisphere. These winds contain huge amounts of kinetic energy, or the energy contained in any fluid body in motion. Approximately 2% of the solar energy that strikes the Earth is converted into wind. For various reasons, including the revolution of Earth and the features of its terrain, some parts of the Earth have more wind than the others.

Using Wyoming as an example of a state with ample potential for the occurrence of wind (almost daily – the famed Wyoming breeze is a 25 mph wind), there are large wind farms that consist of hundreds of individual wind turbines that are connected to the electric power transmission network. On the other hand, the southeastern United States (compared to Wyoming) has relatively little wind on a regular basis, so this region is generally not considered a good place to place wind turbines. In addition, the storminess in the Southeast would leave wind turbines vulnerable to damage from high winds, during hurricane season, for example. The Rocky Mountain states experience a great deal of wind on a consistent basis, making them better candidates for wind power. The best places to build the turbines are North Dakota, Texas, and Kansas, which by themselves could provide all of the electricity needed in the United States.

Large wind farms consist of hundreds of individual wind turbines that are connected to the electric power transmission network. For new constructions, onshore wind is a relative inexpensive source of electricity, while small onshore wind farms provide electricity to isolated locations. Utility companies increasingly buy surplus electricity produced by small domestic wind turbines. Offshore wind is steadier and stronger than on land, and offshore farms have less visual impact, but the construction and maintenance costs are considerably higher. Floating wind farms are similar to a regular wind farm, but the difference is that they float in the middle of the ocean. Offshore wind farms

can be placed in water up to 130 feet deep, whereas floating wind turbines can float in water up to 2,300 feet deep. The advantage of having a floating wind farm is to be able to harness the winds from the open ocean. Without any obstructions such as hills, trees, and buildings, winds from the open ocean can reach up to speeds twice as fast as coastal areas.

For new constructions, onshore wind is a relatively inexpensive source of electricity, while small onshore wind farms provide electricity to isolated locations. Utility companies increasingly buy surplus electricity produced by small domestic wind turbines. Offshore wind [as evidenced in Ostport (east of Copenhagen, Denmark)] is steadier and stronger than on land, and offshore farms have less visual impact, but the construction and maintenance costs are considerably higher. Floating wind farms are similar to a regular wind farm, but the difference is that they float in the middle of the ocean. Offshore wind farms can be placed in water up to 130 feet (40 meters) deep, whereas floating wind turbines can float in water up to 2,300 feet (700 meters) deep. The advantage of having a floating wind farm is to be able to harness the winds from the open ocean. Without any obstructions such as hills, trees, and buildings, the winds from the open ocean can reach up to speeds twice as fast as coastal areas.

Nighttime wind power is considered the most economical form of electrical power with which to synthesize fuel, because the load curve for electricity peaks sharply during the warmest hours of the day, but wind tends to blow slightly more at night than during the day, so, the price of nighttime wind power is often much less expensive than any alternative.

Wind power offers a number of benefits as an alternative to fossil fuels since it is plentiful, renewable, widely distributed, clean, produces no greenhouse gas emissions during operation, and uses little land. The effects on the environment are generally less problematic than those from other power sources.

However, wind power does have a number of drawbacks. Wind speed does not remain constant, so the supply of power may not always be the same as the demand from consumers. Because many of the best locations for wind turbines are far from urban areas, there are problems with distributing the energy. Also, while wind power is clean and renewable, it also raises environmental concerns. Wind power farms require large stretches of land or have to be placed in environmentally sensitive areas such as deserts or on ridgelines. Many people consider wind farms unsightly, a form of visual pollution. A major environmental concern is the effect of wind farms on patterns of bird migration. Many birds have been killed by flying into wind turbine blades.

The main disadvantage of wind power is the fact that wind is unpredictable, inconsistent, and unsteady, as well as the concern that the full costs of harnessing wind power are not cheap and thus rely on government subsidies to be set up and be competitive. There also are aesthetic concerns, with wind farms being considered by some to be an eyesore, whether restricting the normally picturesque view offshore or in rural areas. Furthermore, there are complaints of noise from turbines, and some communities have been required to shut off their turbines during certain times because of the noise. Older-type wind farms have turbines that spin at high speeds and can thus kill wild birds and bats, although this design has changed so newer wind farms largely avoid such a problem.

In summary, the circulation of wind in the atmosphere (which is not always predictable) is driven by the rotation of the Earth and the incoming energy from the Sun (at the surface, warm air rises and colder air sinks) as well as the circulation of the wind in each hemisphere in three distinct cells (the Ferrel Cell, the Hadley Cell, and the Polar Cell) which help transport energy and heat from the equator to the poles, thereby influencing the climate and the availability of wind for power generation. Thus, changes in the Hadley cell and Walker circulation can result in dramatic climate variations for many regions.

See also: Atmosphere, Coriolis Force, Coriolis Force, Ferrel Cell, Hadley Cell, Polar Cell, Wind Power.

Wind Power

Wind is another renewable energy source that has received much attention in recent years. Wind should almost certainly be used more than it is at present, but for fundamental technological reasons, it will not be the ultimate solution to the electricity generation problem. The idea behind wind power is that wind striking the blades of a large windmill causes them to rotate. This rotational kinetic energy, by a series of gears, drives an electric generator producing electricity.

Wind has some important advantages which are (i) wind power is clearly a renewable energy source, (ii) wind produces electricity in a very clean manner insofar as there are no carbon dioxide emissions or any other harmful pollutants, (iii) a steam cycle is not involved and, therefore the conversion from wind kinetic energy to electricity is reasonably efficient, and (iv) the cost of wind power is within a tolerable range which is particularly true if one were to add in the additional environmental costs of fossil fuel plants.

There are, however, some disadvantages to wind power: (i) the wind does not blow at a constant rate – if it is too weak, not much power is produced or if it is too strong, the blades must turn parallel to the wind to prevent them from spinning too fast and causing mechanical failure, (ii) the power intensity of the wind is very low as compared, for instance, to that in the center of a coal furnace, and producing a significant amount of power requires a large number of windmills spread over a large area.

There are several environmental issues to consider. Windmills tend to be noisy and harmful to birds. There is also the issue of aesthetics. Engineers may find beauty in modern windmills, but the general public tends to view them as unattractive eyesores. Also, they are quite large, with mounting towers on the order of 300 feet high and blades that are on the order of 150 feet in length.

See also: Coriolis Force, Ferrel Cell, Hadley Cell, Polar Cell, Weibull Distribution, Wind Energy.

Wind Speed and Wind Gusts

Wind speed is one of the most critical characteristics in wind power generation. In fact, wind speed varies in both time and space, determined by many factors such as geographic and weather conditions – inclusion the Coriolis Force, the Ferrel Cell, the Hadley Cell, and the Polar Cell play a role. Because wind speed is a random parameter, measured wind speed data are usually dealt with using statistical methods.

The diurnal variations of average wind speeds are often described by sine waves. As an example, the diurnal variations of hourly wind speed values have shown the (variable) wavy patterns. Also, based on the wind speed data, it has concluded that the monthly average wind speed in some areas is inversely propositional to the monthly average temperature, i.e., the wind speed is higher in the winter and lower in the summer. In fact, the year-to-year variation of yearly mean wind speeds depends highly on selected locations and thus there is no common correlation to predict it. It is possible, however, to described the wind speed at a site by using the Weibull distribution function which illustrates the probability of different mean wind speeds occurring at the site during a period of time.

One aspect of wind speed that deserves mention here is the phenomenon of wind gust that refers to a sudden increase in wind speed in a relatively small interval of time. In case of sudden turbulent gusts, wind speed, turbulence, and wind shear may change drastically. Reducing rotor imbalance while maintaining the power output of wind turbine generator constant during such sudden turbulent gusts calls for relatively rapid changes of the pitch angle of the blades. However, there is typically a time lag between the occurrence of a turbulent gust and the actual pitching of the blades based upon the dynamics of the pitch control actuator and the large inertia of the mechanical components.

As a result, load imbalances and generator speed, and hence oscillations in the turbine components, may increase considerably during such turbulent gusts, and may exceed the maximum prescribed power output level. Moreover, sudden turbulent gusts may also significantly increase tower fore-aft and side-to-side bending moments due to increase in the effect of wind shear. To ensure safe operation of wind farms, wind gust predictions are desirable.

See also: Coriolis Force, Ferrel Cell, Hadley Cell, Polar Cell, Wind Energy.

Wind Turbines

A wind turbine is a machine which converts the power in the wind into electricity. This is in contrast to the older windmill, which is a machine which converts the power of wind into mechanical power. As electricity generators, wind turbines are connected to some electrical network. These networks include battery-charging circuits, residential-scale power systems, isolated or island networks, and large utility grids.

A modern wind turbine is an energy-converting machine to convert the kinetic energy of wind into mechanical energy and in turn into electrical energy. In the recent decades in the latter part of the 20th century, it has been estimated that advances in aerodynamics, structural dynamics, and micrometeorology may contribute to a 5% annual increase in the energy yield of wind turbines. Various wind turbine concepts have been developed and built for maximizing the wind energy output, minimizing the turbine cost, and increasing the turbine efficiency and reliability.

Thus, a wind turbine captures the kinetic energy of wind with, in most cases, two or three blades shaped much like airplane propellers. These blades are attached to a tower that rises at least 100 feet above the ground. At this height, air currents tend to be stronger but less turbulent than they are at ground level. When the wind strikes the blade, the angle and configuration of the blade form a pocket of low pressure on the downwind side of the blade. This low pressure sucks the blade into movement, causing the rotor to turn. Force is added by the high pressure on the upward side of the blade. In aerodynamic theory, this property is called lift. If the blade is designed correctly, lift is stronger than drag, or the slowing force exerted by the wind on the front of the blade.

In wind turbines, lift and drag work together to make the entire mechanism spin like a propeller. In earlier windmills, drag rather than lift was the force that turned the blades. The process is the opposite of that of a fan. With a fan, electricity is used to make wind. With a wind turbine, wind is used to produce electricity. The turning rotor of a wind turbine is connected to a shaft, which is connected to an electric generator. Power can be distributed to users over the electric grid in exactly the same way any other electric power is distributed. The most important feature in the operation of wind turbines is lift. To achieve lift, wind turbine designers have borrowed technology from aircraft designers. In cross section, an airplane wing looks like an irregularly shaped teardrop. The shape is irregular because the wing's bottom is slightly flatter than the top, which is more curved. When a plane flies, its wings slice through the air, creating wind. Because of the curve of the upper surface of the wing, the air has to flow faster to get around the wing. At the same time, the air flows at a lower speed along the bottom surface of the wing. Because of the difference in speed, the air above the wing is less dense; that is, the air pressure is lower than the pressure of the air below the wing. This difference in pressure creates lift perpendicular to the direction of the moving air, allowing the plane to fly. The same principle applies to turbine blades. Unlike airplane wings, wind turbine wings are almost always twisted. The reason they are twisted has to do with another aerodynamic principle, stall. When an airplane wing is tilted back, the wind continues to flow smoothly along the bottom surface, but along the top surface, because of the steeper angle presented to the wind, the air no longer sticks to the wing but swirls around in a circle above it. The result of this swirling is the loss of the low pressure along the upper surface of the wing. Without this low pressure, the plane has no lift and drops like a rock.

Unlike airplane wings, wind turbine blades are constantly rotating, and the speed of the rotation differs along the entire length of the blade. At the precise geometric center, the speed of rotation is zero. This speed steadily increases along the length of the blade until at the tip; the blade can be moving hundreds of feet (meters) per second. This rotation changes the direction at which the wind hits the blade all along its length. In effect, the angle at which the wind hits the blade would be different at each point along the blade if the blade were not twisted. When the blade is twisted, the angle at which the wind hits the blade is the same at each point, and stall is eliminated under normal wind conditions. Excessively high wind speeds can damage rotors, however, so engineers have designed blades that stall when the wind is too strong, and the rotor stops spinning.

There are two main configurations for wind turbines: (i) the horizontal axis turbine and (ii) the vertical axis turbine. The horizontal axis wind turbine (HAWT) and the vertical axis wind turbine (VAWT) are classified or differentiated by the axis of rotation the rotor shafts. Thus, horizontal axis wind turbine (also known as the Darrieus wind turbine) has a horizontal rotor shaft and an electrical generator which is both located at the top of a tower, while the vertical axis wind turbines are designed with a vertical rotor shaft, a generator, and gearbox which are placed at the bottom of the turbine, and a uniquely shaped rotor blade that is designed to harvest the power of the wind no matter which direction it is blowing. Also, the horizontal axis wind turbine rotors are usually classified according to the rotor orientation (upwind or downwind of the tower), hub design (rigid or teetering), rotor control (pitch vs. stall), the number of blades (usually two or three blades), and how they are aligned with the wind (free yaw or active yaw).

A yaw rotation is a movement around the yaw axis of a rigid body that changes the direction it is pointing, to the left or right of its direction of motion. The yaw rate or yaw velocity is the angular velocity of the rotation, or rate

of change of the heading angle when the machine is horizontal. It is commonly measured in degrees per second or radians per second.

A typical modern wind turbine, in a wind farm configuration, and the actual conversion process use the basic aerodynamic force of lift to produce a net positive torque on a rotating shaft, resulting first in the production of mechanical power and then in its transformation to electricity in a generator. Wind turbines, unlike most other generators, can produce energy only in response to the resource that is immediately available. It is not possible to store the wind and use it at a later time. The output of a wind turbine is thus inherently fluctuating and non-dispatchable.

Any system to which a wind turbine is connected must, in some way, take this variability into account. In larger networks, the wind turbine serves to reduce the total electrical load and thus results in a decrease in either the number of conventional generators being used or in the fuel use of those that are running. In smaller networks, there may be energy storage, backup generators, and some specialized control systems. A further fact is that the wind is not transportable: it can only be converted where it is blowing. Historically, a product such as ground wheat was made at the windmill and then transported to its point of use.

Almost all wind turbines use either induction or synchronous generators. These designs entail a constant or nearly constant rotational speed when the generator is directly connected to a utility network. If the generator is used with power electronic converters, the turbine will be able to operate at variable speed.

Many wind turbines installed in grid-connected applications use squirrel cage induction generators (SQIG) which operate within a narrow range of speeds slightly higher than its synchronous speed (a four-pole generator operating in a 60 Hz grid has a synchronous speed of 1,800 rpm). The main advantages of this type of induction generator are that it is rugged, inexpensive, and easy to connect to an electrical network. An increasingly popular option is the doubly fed induction generator (DFIG) which is often used in variable-speed applications.

An increasingly popular option for utility-scale electrical power generation is the variable speed wind turbine. There are a number of benefits that such a configuration offers, including the reduction of wear and tear on the wind turbine and potential operation of the wind turbine at maximum efficiency over a wide range of wind speeds, yielding increased energy capture. Although there are a large number of potential hardware options for variable-speed operation of wind turbines, power electronic components are used in most variable-speed machines currently being designed. When used with suitable power electronic converters, either synchronous or induction generators of either type can run at variable speed.

The principal types of tower design currently in use are the free-standing type using steel tubes, lattice (or truss) towers, and concrete towers. For smaller turbines, guyed towers are also used. Tower height is typically 1 to 1.5 times the rotor diameter, but in any case is normally at least 60 feet. Tower selection is greatly influenced by the characteristics of the site. The stiffness of the tower is a major factor in wind turbine system dynamics because of the possibility of coupled vibrations between the rotor and tower. For turbines with downwind rotors, the effect of tower shadow (the wake created by air flow around a tower) on turbine dynamics, power fluctuations, and noise generation must be considered. For example, because of the tower shadow, downwind turbines are typically noisier than their upwind counterparts.

Wind power has grown to be economically competitive with other forms of power. Although it costs more to generate 1 kilowatt of electricity by wind power than it does with coal- or oil-fired generators, the gap is closing. If 20% of a family's electricity were to come from wind power, the electric bill would be less than \$2 higher per month. The cost of generating wind power has decreased by 85% since 1980.

Wind turbines do not consume water, making them ideal for dry or drought-stricken areas. In contrast, conventional and nuclear power plants consume large amounts of water for cooling and other purposes. Also, wind power is homegrown and not subject to inter-political differences of opinion between countries (as is the case with crude oil) and because wind is free, consumers are not at the mercy of frequently increasing fuel prices.

Wind power is inexhaustible and renewable, in contrast to fossil fuels, and it is clean. Wind power does not contribute to acid rain, smog, global warming, or mercury contamination. It does not release dangerous particles into the air. Also, wind energy is safe. Although the risk exists for industrial accidents in the construction of a wind turbine, the same can be said related to the construction of any facility. The risk that the public will be harmed by a wind-power facility is nearly zero. With nuclear power, the risk of catastrophe is ever present, and with fossil fuel plants, the danger from fire and explosions is high.

On the negative side, wind turbines can be noisy, and engineers are working on ways to quiet the noise. The best method has been to reduce the thickness of the trailing edges of blades. Noise also has been reduced by placing turbines in an upwind rather than a downwind position. The wind hits the blades first, then the tower, rather than the other way around, eliminating the thumping sound that downwind designs make as the blade passes the wind shadow cast by the tower.

Wind farms require a fair amount of land, approximately 60 acres per megawatt of electrolyte produced. However, the turbines themselves plus service roads occupy only approximately 3 acres of the 60 acres. Once the turbines have been built, farmers and ranchers can continue to use the land under them for traditional purposes. Land is difficult to find near larger cities. One solution to this problem is to place wind turbines in shallow waters offshore where possible.

In many regions, the wind is intermittent, meaning that wind power has to be supplemented by other forms of power. Wind-power generation poses additional challenges for power-grid managers, who have to ensure that enough power is available to meet peak demand at all times, even when the wind is not blowing. Thus, not all areas of any country are suitable for wind-power generation. Wind towers and rotors can interfere with radar, posing a potential hazard for air travelers. They can also interfere with television and radio transmission, particularly if they are in the line of sight between the signal source and the receiver. Finally, wind turbines can be a hazard to birds, which sometimes fly into the rotors.

The use of wind power benefits the environment, because this form of energy is clean and it does not consume water. On the other hand, wind power can have harmful effects on the environment. Some environmentalists are concerned about soil erosion, particularly in desert regions, where a thin, fragile layer of topsoil would be disturbed in the construction of turbines, and in the eastern United States, where turbines would be built on mountain ridgelines. Good engineering practices could lessen these effects.

Another potential problem is the effects of wind farms on bird life since birds and bats sometimes fly into wind-turbine blades and are killed; this problem is site specific. Environmentalists are also concerned that wind farms with their service roads and transmission lines may break up the habitat of birds and other wildlife.

See also: Mechanical Energy, Weibull Distribution, Wind Energy, Wind Speed and Gusts.

Wind Turbines – Classification

Wind turbines can be classified according to (i) the turbine generator configuration, (ii) the airflow path relative to the turbine rotor, (iii) the turbine capacity, (iv) the generator-driving pattern, (v) the power supply mode, and (vi) the location of turbine installation.

When considering the configuration of the rotating axis of rotor blades, modern wind turbines can be classified into the (i) horizontal-axis turbines and (ii) vertical-axis turbines. Many modern commercial wind turbines belong to the horizontal-axis type, in which the rotating axis of blades is parallel to the wind stream. The advantages of this type of wind turbines include the high turbine efficiency, high power density, low cut-in wind speeds, and low cost per unit power output.

The blades of the vertical-axis wind turbines rotate with respect to their vertical axes that are perpendicular to the ground. A significant advantage of the vertical-axis wind turbine is that the turbine can accept wind from any direction and thus no yaw (the twisting or oscillation about a vertical axis) control is needed. Since the wind generator, gearbox, and other main turbine components can be set up on the ground, it greatly simplifies the wind tower design and construction, and consequently reduces the turbine cost. However, the vertical-axis wind turbines must use an external energy source to rotate the blades during initialization. Because the axis of the wind turbine is supported only on one end at the ground, the maximum practical height is limited. Due to the lower wind power efficiency, vertical-axis wind turbines today make up only a small percentage of wind turbines.

Based on the configuration of the wind rotor with respect to the wind flowing direction, the horizontal-axis wind turbines can be further classified as upwind and downwind wind turbines. The majority of horizontal-axis wind turbines in use are upwind turbines, in which the wind rotors face the wind which offers the advantage of avoiding the distortion of the flow field as the wind passes through the wind tower and nacelle (a streamlined housing or tank). For a downwind turbine, wind blows first through the nacelle and tower and then the rotor

blades and this configuration enables the rotor blades to be made more flexible. However, because of the influence of the distorted unstable wakes behind the tower and nacelle, the wind power output generated from a downwind turbine fluctuates. In addition, the unstable flow field may result in more aerodynamic losses and introduce more fatigue loads on the turbine. Furthermore, the blades in a downwind wind turbine may produce higher impulsive or thumping noise.

See also: Mechanical Energy, Wind Turbines.

Wind Turbines – Environmental Impact

Modern wind farms today may contain a large number of large-size wind turbines. Therefore, their impacts on the environment cannot be ignored. One of the impacts is that poorly sited wind energy facilities may block bird migration routes and hurt or kill birds. Though blade rotation speeds are rather low for large wind turbines at their normal operation, the tangential speeds at the blade tips could be higher than 70 meters per second. At such high speeds, birds flying through the blade sweeping areas may be easily hurt or killed by colliding with blades. It is important to evaluate the long-term influence on local geography, seasonal bird abundance, and the species at risk. To reduce the bird death, using bird scares to drive birds away from wind farms has been considered.

Before building a wind farm, a series of environmental assessments have to be completed to avoid bird migration routes and to minimize other environmental impacts. Once the wind farm is built, further monitoring takes place to better understand the ongoing relationship between birds and the wind farm. Building wind farms will change the character of local landscape. Modern large wind turbines are more than 300 feet tall and thus can be seen at a far distance. In practice, the visual effect for local residents is a significant consideration and is always scrutinized for wind projects. To minimize the visual effect, wind turbines usually use neutral colors such as light gray or off-white. Strategies to minimize visual effects involve the spacing, design, and uniformity of turbines, markings or lighting, roads, and service buildings.

With the extensive buildup of wind power plants, the influence of wind turbine noise to the nearby residents becomes an issue that cannot be ignored. Wind turbine noise consists of aerodynamic noise from rotating blades and mechanical vibration noise from gearboxes and generators. For a modern large wind turbine, aerodynamic noise from the blades is considered to be the dominant noise source. There are two components in aerodynamic noise which are (i) airfoil self-noise, that is, the noise produced by the blade in an undisturbed inflow and is caused by the interaction in the boundary layer with the blade trailing edge; and (ii) inflow turbulence noise which is caused by the interaction of upstream atmospheric turbulence with the blade and depends on the atmospheric conditions. Both airfoil self-noise and inflow turbulence noise mechanisms are dependent on a number of parameters such as wind speed, angle of attack, radiation direction, and airfoil shape.

There are a number of techniques for reducing aerodynamic noise produced by wind turbine blades. One technique is to use serrated blades at the trailing edge of the blades which can improve blade aerodynamic characteristics and reduce the noise induced by a Kármán vortex street, which is a repeating pattern of swirling vortices, caused by a process known as vortex shedding, which is responsible for the unsteady separation of flow of a fluid around blunt bodies.

Another technique is to use turbulence generating means, placed on the leeward surface side and at the outer section of the blade, to reduce noise.

See also: Mechanical Energy, Wind Turbines.

Winkler Gasifier

Another gasifier that has had wide commercial use but is now mainly of historical interest is the Winkler gasifier.

Unlike the other gasifiers discussed so far, the Winkler gasifier is a fluidized bed system. It was the first commercial application of fluidized bed technology, and was developed in the late 1920s with the aim of gasifying coal fines, which were cheaper than lump coal. It operates at atmospheric pressure or slightly above, with a bed temperature of around 950°C. Gasification reactions are similar to the Lurgi except that there is less methane formation due

to the lower pressure, and pyrolysis products including tars and oils are decomposed within the gasifier. Being both a low-pressure and low-temperature process, gasification rates are low and residence times of up to 3 hours are required to achieve acceptable conversions. Carbon conversions are, in fact, as low as 60%, partly due to the difficulty in measuring the coal feed rate, and the need to maintain an excess of coal relative to oxygen for safety considerations. In addition, the fluidized bed system cannot handle caking and swelling coals, and the Winkler is really only suitable for use with the highly reactive lignite for which it was originally intended. Consequently, Koppers-Totzek and Lurgi units are replacing the Winkler in commercial applications.

See also: Gasification, Gasifiers.

Winkler Process

The Winkler process is an established process for the gasification of coal. In the process, dried, crushed coal (-8 mesh) is fed to the fluidized bed gasifier through a variable-speed screw feeder whereupon the coal is contacted with steam and oxygen injected near the bottom of the vessel. The upward flow of steam and oxygen maintains the bed in a fluidized state at a temperature of 815 to 980°C (1,600 to 1,800°F) with a pressure that is marginally higher than atmospheric. The high operating temperature reduces the amount of tars and other heavy hydrocarbons in the product.

Approximately 70% of the coal ash is carried over by the gas flow, and the remainder is removed from the bottom of the vessel by screw conveyors. Unreacted carbon contained in the carryover ash is consumed by the injection of supplemental steam and oxygen in the space above the bed. In order to moderate the bed temperature and thereby minimize ash melting, a heat exchange surface is provided in the dilute phase to remove heat and generate steam. The raw gas leaving the gasifier, rich in carbon monoxide and hydrogen, is cooled to approximately 705°C (1,300°F) in a boiler and then passes through (i) a heat exchanger to superheat steam, (ii) a waste heat boiler, and (iii) a cyclone to remove entrained char. Further gas clean-up is affected by wet scrubbers, electrostatic precipitators, and sulfur removal technology.

See also: Gasification, Gasifiers.

Wobbe index

The Wobbe index (WI, or Wobbe number, WN) is a number which represents the properties of a stream gas and is the calorific value of a gas divided by the specific gravity. The Wobbe Index is an indicator of the interchangeability of fuel gases such as natural gas, liquefied petroleum gas (LPG), and coal gas. It is frequently defined in the specifications of gas supply and transport utilities.

The Wobbe Index, I_w , is the relationship between the higher heating value and the square root of gas specific gravity:

$$I_w = V_c / \sqrt{G_s}$$

V_c is the higher heating value, or calorific value, and G_s is the specific gravity.

The higher heating value (HHV; also known as the gross calorific value or gross energy) of a fuel is the amount of heat released during combustion by a specified quantity (initially at 25°C), and the products have returned to a temperature of 25°C. The *higher heating value* takes into account the latent heat of vaporization of water in the combustion products, and is useful in calculating heating values for fuels where condensation of the reaction products is practical (e.g., in a gas-fired boiler used for space heat) and assumes all the water component is in liquid state at the end of combustion (in the product of combustion).

The lower heating value (net calorific value, net CV, or LHV) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C or another reference state) and returning the temperature of the combustion products to 150°C.

The lower heating value assumes all the water component is in vapor state at the end of combustion (in product of combustion), as opposed to higher heating value which assumes the entire water component in the liquid form of the combustion gas. The lower heating value assumes that the latent heat of vaporization of water in the fuel and the reaction products is not recovered. It is useful in comparing fuels where condensation of the combustion products is impractical, or heat at a temperature below 150°C cannot be put to use.

The Wobbe Index (Table W-6) is used to compare the combustion energy output of different composition fuel gases in an appliance (fire, cooker, etc.). If two fuels have identical Wobbe Indices, then for given pressure and valve settings, the energy output will also be identical. Typically, variations of up to 5% are allowed as these would not be noticeable to the consumer. The Wobbe Index is a critical factor to minimize the impact of the changeover when analyzing the use of synthetic natural gas fuels such as propane-air mixtures.

Table W-6 Wobbe index (kcal/m³) of natural gas and its common constituents.

Gas	Upper Index	Lower Index
Natural gas	12,837	11,597
Methane	12,735	11,452
Ethane	16,298	14,931
Propane	19,376	17,817
n-Butane	22,066	20,336
iso-Butane	21,980	20,247

The Wobbe index is commonly expressed in Btu per standard cubic foot or megajoules per standard cubic meter (1000 BTU/scf = 37.3 MJ/m³). In the case of natural gas, the typical heating value is around 1,050 Btu per cubic foot and the specific gravity is approximately 0.59, giving a typical Wobbe index of 1.367.

There are three ranges or groups of fuel gases that have been internationally agreed based on Wobbe Index which are (i) Group 1, which includes manufactured gases, (ii) Group 2, which covers natural gas, with high and low ranges, and (iii) Group 3, which includes liquefied petroleum gas (LPG).

Combustion equipment is typically designed to burn a fuel gas within a particular family: hydrogen-rich town gas, natural gas, or liquefied petroleum gas. Other flame characteristics and composition limits may determine the acceptability of the replacement gas, e.g., flame speed, yellow tipping due to incomplete combustion, sulfur content, and oxygen content.

Wood

Of all of the alternate energy sources (relative to fossil fuels), the use of wood predates the others and dates from pre-biblical times (pre-4,000 BC). In peace and in war, in the Old and the New World, man first turned to wood for his basic needs and later learned to use advanced science to employ wood as his most sophisticated raw material, being infinitely versatile and an easily renewable source.

The manner in which wood was used by early cultures is difficult to determine, as wood artifacts have largely disappeared. Certainly, the use of wood for fire is one of the first and most significant contributions of this resource to the development of society. No doubt man built early pole structures from the small trees growing along the rivers, and later, he would build more solid structures from planks, turf, mud, and adobe. The Scandinavians developed the basic principles of timber framing which were probably known in Europe in the Bronze Age, and framing eventually became the pre-eminent method of wood building in the Western World, reflecting developments in structural engineering that had been worked out with wood mostly through trial and error.

One of the first uses of wood for water transport was probably a hollowed-out log. Around 4000 BC, the Egyptians were making ships from bundles of reeds and their earliest wooden boats copied the hull frame of the reed boats.

For larger vessels, the Egyptians imported cedar from Lebanon. One reason for the northward expansion of Egypt's influence was to ensure its cedar supply. Records show that the Egyptian shipbuilder could use wood on a grand scale. Queen Hatshepsut's barge, built in 1500 BC to transport granite obelisks from Aswan to Thebes, had a displacement of some 7500 tons, and 30 oar-powered tugs were needed to tow it.

According to Theophrastus, a pupil of Aristotle, there is knowledge of the shipbuilding in Ancient Greece and the ship-building woods are silver fir, fir, and cedar. Silver fir is used for lightness; for merchant ships, fir is used because of its resistance to rot. In Syria and Phoenicia, cedar is used because of the lack of fir.

Technological improvement in land transport was slower than that of water transport. From 7000 B.C. onward, wood sledges were used for heavy loads such as stones, and archeologists reason that the massive stones in the great monument at Stonehenge on Salisbury Plain, England, must have been moved on sledges placed on rollers, which may have inspired the discovery of the wheel. But there is still no record of when and where the wheel was invented, though surely the first axle was made of wood.

Another significant contribution of wood to the ancient world was for war devices. Examples include the catapult, which enabled a man to attack his enemy from a safe distance, the battering ram and scaling ladder, the tortoise, and the siege tower. Although the choice of materials for these purposes was quite limited, the properties of wood made it eminently suitable. High strength and low weight were highly valued characteristics of wood then, just as they are today. These siege engines were integral to the expansion of both Greek and Roman civilizations and of the science, technology, and philosophy that developed under the tutelage of the great thinkers and teachers of the times.

The ancient man was using wood to conquer his world as well as build it and explore it. Then, some unknown woodman in Ancient Greece invented a primitive wooden lathe, and man found himself on the threshold of the age of machines. When he entered that age, he would find ways to make wood work for him to unprecedented degrees. From the basic concept of the lathe and the ability to shape wood to circular symmetry developed new concepts of both materials use and machine development.

In Europe, the water-and-wood phase reached a high plateau around the 16th century. At about this time, the availability of timber diminished. The scarcity was caused by the expansion of agriculture, the increasing use of wood as a structural material and fuel, and from growing demands of the smelting furnaces. To smelt one cannon took several tons of wood. By the 17th century, Europeans were turning to coal for the domestic hearth, and when the secret of smelting metal with coal was discovered, coal became the unique basis for industrial technology until late in the 19th century.

In early 19th century America, a seemingly inexhaustible supply of timber existed. The technology here was geared to exploiting the use of all natural resources to make up for the scarcity in capital and labor. But the technological advances of the 19th century, along with the increasing population, would have a major impact on American forests. Railroads, telegraph lines, charcoal-fueled steel mills, and other industries were consuming immense quantities of wood. The Civil War made a heavy demand – for example, one gun factory alone used 28,000 walnut trees for gun-stocks. During the latter half of the 19th century, the volume of lumber produced each year rose from 4 thousand million board feet to approximately 35 thousand million board feet.

As with many other industries of this time, lumbering was a highly competitive business. Quick profits were the name of the game. This encouraged careless and extravagantly wasteful harvesting and manufacturing methods. The visible devastation that resulted encouraged a new concern for America's forests. Theories were published that purported to prove that the fall of ancient empires, radical changes of climate, and the spread of epidemics could be attributed to deforestation.

However, the wood-and-water phase in the United States reached its own plateau around 1850 and approximately 200 years after that phase had peaked in Europe. The European technology was based on the coal-and-iron complex. Some of the traditional uses of wood – for fuel, pavement, sailing ships, charcoal, and iron smelting – were taken over by coal, steel, and stone. However, demand for timber was maintained as many new uses as possible of wood, for paper, plywood, telegraph and telephone poles, railroad ties, and chemicals, entered the picture. The selection from among competing materials was based partly on cost and availability and partly on properties and performance. It is also noteworthy that such a range of choices coincided with the rapid mechanization and increasing technical complexity of society. Nevertheless, in the late 19th century, the use of wood products had begun to level off. For the time being, most of the country stopped worrying about a timber scarcity. Coal was abundant, and iron and steel could be manufactured.

Up to the latter part of the 19th century, no appreciable systematic research on wood occurred. Wood had been used by early experimenters to make instruments and other research equipment, and early engineers had used it as a

construction material and a material with which to work out engineering problems and designs. Methods for pulping wood to make paper had been worked out by the paper industry, too. Further, both cotton and wood had been used by chemists as a source of cellulose for man-made fibers. This led to work on cellulose acetate reactions with solvents that led to the ability to produce that compound as both film and fiber. These advances provided a base for the subsequent technology of nylon and established the principles by which countless numbers and kinds of linear high polymers can be synthesized.

The carriage business provided an early milestone for a new era of wood research. In 1889, the Carriage Builders Association was concerned about the scarcity of northern oak, a species long preferred for their craft. The builders wondered if southern oak, in plentiful supply, possessed the same desirable characteristics as the northern species. The Division of Forestry of the US Department of Agriculture stepped in to help solve the problem. Its research confirmed that a suitable material could be obtained from the South as well as the North. This incident was an important step toward comprehensive wood research as is known currently. From 1890 to 1910, small amounts of money were appropriated by the Division of Forestry to universities for wood research. Studies of the mechanical properties of wood were begun, along with wood preservation and wood drying studies.

In 1910, the Division of Forestry, in cooperation with the University of Wisconsin, established the world's first comprehensive forest products-laboratory in Madison, Wisconsin, to centralize the federally sponsored wood science efforts in the country. The birth of a full-fledged wood research laboratory could not have happened much earlier. The leaps and bounds science had taken in the 19th century provided the necessary foundation for such a laboratory. Each of the major branches of experimental science made such great progress then that in retrospect, its earlier state seemed rudimentary. Scientists would call this century the Golden Age.

During World War II, wood research covered the whole gamut of possible wartime uses of wood, but after the war the importance of timber products declined, on a relative scale, as the importance of minerals increased, due in part to abundant low-cost energy in the form of coal and then petroleum. It is worth noting, however, that the tonnage of timber products produced in the USA then exceeded that of all metals and plastics combined, just as it does today. So, while timber declined in relative importance and public awareness, it remained the major product of American manufacture.

Currently, low cost and accessible energy can no longer be taken for granted and there are many people, including materials scientists and engineers, who are beginning to appreciate the need for renewable resources like wood. This appreciation is heightened and fed by the fact that the USA finds itself blessed with a timber inventory that is increasing each year. Unfortunately, much of this is not of the large clear sixes and high quality to which humans are accustomed.

On the other hand, the past abundance of timber and the dispersion of the industry have worked against advances in technology for the efficient production, conversion, and use of wood products. Fortunately, and despite its relatively recent origin as a recognized field of study, wood science has had an appreciable effect on wood technology as well as science in general. The study of wood chemistry has contributed to an understanding of the principal components of wood – cellulose and lignin – and their reactions. Early research on hydrolysis of cellulose was prompted by fuel needs in World War I, but contributed much to the knowledge base of this form of chemical reaction. Similarly, research on nitrocellulose was prompted by the needs for explosives. Accompanying studies of saccharification and fermentation are contributing much to scientific knowledge in those areas. Engineering studies of wood as an orthotropic material contributed strongly to the concept of sandwich construction, now commonly used in aircraft design, as well as to the early development of glass-fiber-reinforced plastics in the 1950s and 1960s.

Another research focus is on use of wood for fuel, which still plays a big part in man's existence. Today, approximately half of the world's annual wood harvest is burned for those same products the primitive man valued from his wood fire – heat and light. But much of this is in the less developed countries. In most developed countries, the use of wood for fuel peaked in the last century. But with the energy situation as it is today, even developed countries are turning to wood for fuel. It is renewable, relatively cheap, low in ash content, and negligible in sulfur content.

On the other hand, wood is bulky, has less than half the heat of combustion of fuel oil, and in its green state is heavy to ship. Furthermore, the cost of a wood-burning system may be three to four times that of a gas-burning installation because of fuel storage, handling, and air quality control systems. These drawbacks have kindled interest in production of liquid and gaseous fuels from wood. Much research is devoted to improving existing technology and devising new approaches, but such fuels are still expensive compared with petroleum-based fuels.

Closely related to the conversion of wood to liquid or gaseous fuel is the use of the chemical storehouse that is wood to produce a wide range of silvi-chemicals. Research has shown how to produce useful products from cellulosic

polymers, wood and bark extractives, oleoresins, and pulping liquors. Many processes of these types already form the basis of chemical production on a commercial scale. But the potential to use wood as a chemical feedstock is much greater than has so far been realized. Whole wood can be gasified, liquefied, or pyrolyzed in ways comparable with those used for coal to yield a wide variety of chemicals. Cellulose, as a glucose polymer, can be hydrolyzed to the glucose monomer by acid or enzymes, and the glucose then fermented to ethanol. The ethanol can be used as a fuel or as a source of other important chemicals such as ethylene or butadiene.

As an alternative, the use of glucose as a substrate for fermentation would make a possible production of antibiotics, vitamins, and enzymes. Hemicelluloses can easily be converted to simple sugars which can be used to produce ethanol or furfural, a potential raw material for nylon or other synthetics.

Lignin can be pyrolyzed, hydrogenated, and hydrolyzed to yield phenols, which can be further processed to benzene. Once the technology and economics are feasible, future plants will manufacture a variety of these significant chemicals from wood, now derived from petroleum or other resources.

See also: Lignin, Lignocellulose, Wood Biomass.

Wood – Biomass

Wood logs are the first ever-known energy application of biomass – burning wood for heating and lighting has been known by humanity for millennia. Stem wood is a perfect feedstock for biomass-to-liquids processing, since being a pure wood (a hydrocarbon material), it has negligible content of impurities and harmful substances that have to be removed during gasification compared to, e.g., waste wood.

The wood biomass comprises stem wood from ordinary forestry, dedicated (short-rotation) forestry, as well as various residues and wood wastes. However, two core types of biomass raw material are distinguished: (i) woody biomass and (ii) herbaceous biomass. Currently, woody material accounts for approximately 50% of the total world bioenergy potential. Another 20% is straw-like feedstock, obtained as a by-product from agriculture. However, wood from different sources will exhibit different properties (Table W-7).

Table W-7 Examples of the properties of different types of wood.

Property	Wood	Forest residue	Wood chips	Wood pellets
Proximate analysis				
Ash, % w/w	0.4-0.5	1-3	0.8-1.4	0.4-1.5
Moisture, % w/w	5-60	50-60	20-50	7-12
Volatile matter, % w/w w/	>70	>70	76-86	>70
Ash melting point, °C	1,400-1,700	-	1,000-1,400	>1,120
Elemental analysis				
C, % w/w	48-52	48-52	47-52	48-52
H, % w/w	6.2-6.4	6.0-6.2	6.1-6.3	6.0-6.4
N, % w/w	0.1-0.5	0.3-0.5	<0.3	0.27-0.9
O, % w/w	38-42	40-44	38-45	40
S, % w/w	<0.05	<0.05	<0.05	0.04-0.08
Cl, % w/w	0.01-0.03	0.0-1-0.04	0.02	0.02-0.04
K, % w/w	0.02-0.05	0.1-0.4	0.02	-
Ca, % w/w	0.1-1.5	0.2-0.9	0.04	-

The technical platform chosen for biofuel production is determined in part by the characteristics of the biomass available for processing. The majority of terrestrial biomass available is typically derived from agricultural plants and from wood grown in forests, as well as from waste residues generated in the processing or use of these resources. Today, the primary barrier to utilizing this biomass is generally recognized to be the lack of low-cost processing options capable of converting these polymers into recoverable base chemical components.

At present, wood is the largest single renewable energy source in many countries, especially the countries of the European Union, and accounts for more than half of all renewable energies. The woody biomass comprises stem wood from ordinary forestry, dedicated (short-rotation) forestry, as well as various residues and wood wastes.

In the United States, much of the biomass being used for 1st-generation biofuel production includes agricultural crops that are rich in sugars and starch. Because of the prevalence of these feedstocks, the majority of activity toward developing new products has focused on the bioconversion platform. Bioconversion isolates sugars from biomass, which can then be processed into value-added products. Native sugars found in sugarcane and sugar beet can be easily derived from these plants, and refined in facilities that require the lowest level of capital input. Starch, a storage molecule which is a dominant component of cereal crops such as corn and wheat, is comprised wholly of glucose. Starch may be subjected to an additional processing in the form of an acid- or enzyme-catalyzed hydrolysis step to liberate glucose using a single family of enzymes, the amylases, which makes bioconversion relatively simple. Downstream processing of sugars includes traditional fermentation, which uses yeast to produce ethanol; other types of fermentation, including bacterial fermentation under aerobic and anaerobic conditions, can produce a variety of other products from the sugar stream.

Forest biomass or agricultural residues are almost completely comprised of lignocellulosic molecules (wood), a structural matrix that gives the tree or plant strength and form. This type of biomass is a prime feedstock for combustion, and indeed remains a major source of energy for the world today. The thermochemical platform utilizes pyrolysis and gasification processes to recover heat energy as well as the gaseous components of wood, known as synthesis gas or 'syngas'. Syngas can then be refined into synthetic fuels, including Fischer-Tropsch, methanol, and ethanol, through the process of catalytic conversion.

Lignocellulose is a complex matrix combining cellulose, hemicellulose, and lignin, along with a variable level of extractives. Cellulose is comprised of glucose, a six-carbon sugar, while hemicellulose contains both five- and six-carbon sugars, including glucose, galactose, mannose, arabinose, and xylose. The presence of cellulose and hemicellulose therefore makes lignocellulose a potential candidate for bioconversion. The ability of the bioconversion platform to isolate these components was initially limited, as the wood matrix is naturally resistant to decomposition. Recent advances, however, have made this process more commercially viable. Costs remain higher than for starch-based bioconversion, but there is added potential for value-added products that can utilize the lignin component of the wood.

In order to incorporate all aspects of biofuel production, including the value of co-products and the potential of the industry to diversify their product offering, the biorefinery concept is employed. The biorefinery concept is important because it offers many potential environmental, economic, and security-related benefits to society. Biorefineries provide the option of co-producing high-value, low-volume products for niche markets together with lower-value commodity products, such as industrial platform chemicals, fuels, or energy, which offsets the higher costs that are associated with processing lignocellulose.

The wood biomass comprises stem wood from ordinary forestry, dedicated (short-rotation) forestry, as well as various residues and wood wastes. However, two core types of biomass raw material are distinguished which are (i) woody and (ii) herbaceous. Currently, woody material accounts for approximately 50% of total world bioenergy potential. Another 20% is straw-like feedstock, obtained as a by-product from agriculture.

Residual wood is the material that is a refuse without objective value within a specific context; otherwise, it constitutes a material at the end of its usefulness. Thus, a number of woody materials can be included in the group of residues and waste: thinning and logging residues from forest industry (tops, branches, and small size stems), demolition wood and railway sleepers, fiberboard residues, cutter shavings, and plywood residues. Residual woody material is believed to be a very promising bioenergy resource since it is available at much lower or negligible cost compared to wood logs and short-rotation forestry.

However, the availability of residual woody biomass depends on the primary wood yield and typically accounts for 25 to 45% of all harvested wood on average. The heterogeneous composition of the residual and waste woody

biomass (content of moisture, impurities, etc.) might sometimes preclude its application for biomass-to-liquids production. Hence, preliminary treatment of the residual and waste woody biomass may be necessary, in order to make it appropriate for processing to liquid fuels.

Fireplaces and wood stoves, popular aesthetic accessories of the recent past, are rapidly gaining prominence as primary or supplemental heat sources for homes. The rising costs, and in some instances, actual shortages of conventional home heating energies, have led to greatly increased utilization of wood as a heating fuel.

Firewood, one of nature's most common methods of storing solar energy, is a renewable energy source. It is a relatively clean, efficient, safe energy source having low sulfur content and is generally found throughout the country. Its primary products of combustion are carbon dioxide, water vapor, and ash. The ash content is low – only 1 to 2% by weight – and that which does remain can be used as a worthwhile soil conditioner.

A wood fire is easy to start and produces a large quantity of heat in a short time as well as adding a cheerful atmosphere to the home. An ample air supply to the wood fire is important to ensure complete burning or combustible gases. Wood fires are ideal where heat is required only occasionally, for warming a living area on cool days or for supplying extra heat in extremely cold weather. When considering wood as a primary heat source, several factors must be carefully weighed to ensure satisfactory results and acceptable deficiencies.

Generally, hardwoods which provide long-burning fires contain the greatest total heating value per unit of volume. Softwoods which give a fast burning, cracking blaze are less dense and contain less total heating value per unit of volume.

See also: Residual Woody Biomass, Wood, Wood Biomass.

Wood Chips

Wood chips represent a resource that is currently available from forestry, and one of the largest unexploited categories is wood that needs to be removed from forests to reduce the risk of forest fires. Well over 8 billion dry tons of biomass have been identified by the U.S. Forest Service as needing fuel treatment removal. The amount of this biomass potentially available for bioenergy uses is estimated to be approximately 60 million dry tons annually. This estimate takes into consideration factors affecting forest access, residue recovery, and the desirability of using some of the recoverable biomass for conventional wood products. The fraction that could be available for bioenergy and bioproducts is less than 1% of the total size of the fuel treatment biomass resource. Factors affecting the rate at which this source of material will become available include public opinion toward this type of removal, as well as delivered costs and the extent to which technology is developed for utilizing small diameter wood for products other than bioenergy. The other large, underutilized forest sources of woodchips are logging residues and urban wood residues. In both cases, the relatively high costs of removal, handling, and transportation have not compared favorably to their relatively low value as an energy resource. Also, the compost market could compete for urban wood resources.

Wood chips represent chopped with special facilities (chippers) woody raw material – whole trees (usually soft wood), short-rotation forestry, wood residues (branches, tops, etc.) with particle size 5 to 60 mm. The chips from stem wood and short-rotation forestry are of higher quality and contain fewer impurities than the chips from residual and waste woody material, but conversely, they are also more expensive.

Wood chips are gaining an increasing popularity as they allow utilization of various residual and waste woody materials, which otherwise are not suitable for gasification. By combining different woody materials, the poorer qualities of a given material can be partly compensated with the better properties of another material. In addition, chipping ensures a homogeneous feedstock with guaranteed qualities, which is a mandatory pre-requisite for efficient gasification. Chipping is also energy efficient, as it requires only 1-3% of the energy content of woody biomass on average. The energy cost for wetter raw materials is lower, due to their lower internal friction.

As already mentioned, chipping allows a more complete utilization of woody biomass. On the other hand, the reproduction of forests and the maintenance of high wood yields require leaving in the soil part of the nutrients (nitrogen, phosphate, and potassium), contained in wood. A more complete utilization of forest resources also means a larger removal of nutrients. If this process is not carefully controlled, it can result not only in reduced wood yields but also in destroyed biodiversity and deserted areas. It is therefore of prime significance to find the right

balance between short-term yields and long-term fertility of forest soils. Achieving such a balance is relatively easy in practice, since the largest part of the woody biomass, i.e., of the hydrocarbon content, is bound in stems, while the majority of nutrients are contained in needles and branches. Hence, after felling, the whole trees are often left on the ground for a couple of months. During this period, the needles and small branches fall down, owing to gradual drying, and the nutrients are absorbed by the forest soil.

When chipping fresh wood, the moisture content of chips can be high (45 to -55% w/w). Such high moisture levels can obstruct gasification, so the wetness has to be brought down to 5 to 25%. There are three ways of decreasing the moisture content of woody biomass in general and of wood chips in particular, which can be used also consecutively to optimize the financial and energy costs.

When the whole trees are left on the ground for the needles and the small branches to drop away and to remain in the forest, the stems also dry. If the trees are felled between January and March, when the moisture content of wood is normally at its lowest and then are left for the summer to dry, the moisture content can naturally go down from 50-55% to 35-45%. Besides the advantages of natural drying, leaving woody biomass in outdoor storages may result in weight loss, due to natural biological decomposition and/or insect infection (especially for soft wood species). The rate of biological degradation can be rather high, in particular for wet material in the beginning of the storage period. The decomposition rate depends largely on the particle size – the larger the particles, the lower the rate. In order to prevent great weight losses from insect infections, trees left on the ground should be regularly inspected.

Wood chips can be stored outdoor (in the summer) or indoor (in the winter) near the gasification plant for further drying. The summer outdoor storage is preferred, as it is cheaper – due to their low bulk density, chips need large drying space. The reduction of wetness is similar to that of natural drying of whole trees – from 50% to approximately 30%. Outdoor storage of biomass with moisture content less than 30% is not recommended since it can increase due to rainfall. As already stated, in case of outdoor storage and natural drying of chips, special attention should be paid to the rate of biological degradation. Due to the small size of chips, it can be really high – up to 5% per month for fresh chips or bark in the beginning of the period, later on getting down to 1 to 2%.

- Forced drying of wood biomass: Dedicated drying of woody biomass at gasification plants should be avoided in general, since it reduces their energy efficiency and increases costs. Thus, as much as possible, natural drying is recommended. When natural drying is not sufficient and/or heat, which otherwise is lost, is employed for drying (e.g., heat from fuel synthesis), the application of forced drying is justifiable – it even increases the overall energy efficiency of plants. In any case, the additional benefits should be always set against the additional capital and running costs.

See also: Wood, Wood Biomass.

Wood – Combustion

Instead of paying disposal costs, wood combustion for electricity and heat is one way in which forest products companies can utilize their wood residues. However, as with any fire, burning wood fuel creates numerous by-products, some of which may be useful (heat and steam), and others that are undesirable, irritating, or dangerous. Among the deleterious by-products are smoke, containing water vapor, carbon dioxide and other chemicals, and aerosol particulates, including caustic alkali fly ash, which can be an irritating (and potentially dangerous) by-product of partially burnt wood fuel. A major component of wood smoke is fine particles that may account for a large portion of particulate air pollution in some regions.

Typically, wood in a variety of forms, particularly green chips (45% to 50% moisture content on a wet basis), is shipped and maintained at a holding site by the energy plant. Augers or belt conveyors transport the wood chips to the combustor, where they are burned, and the heat of combustion is transferred to a steam or hot water boiler. Steam is converted to electrical power by steam turbines. Excess steam can be used in other plant processes such as, for example, in a dry kiln. Hot water boilers can provide heat to a building through a piping distribution network.

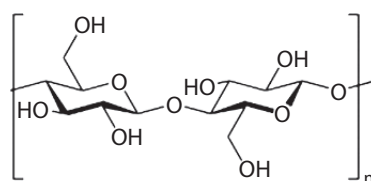
See also: Co-Combustion, Combustion.

Wood – Composition and Properties

Wood consists of cellulose ($C_6H_{10}O_5$), resins, lignin, various inorganic salts, and water. The chemical composition of wood varies from species to species, but is approximately 50% w/w carbon, 42% w/w oxygen, 6% w/w hydrogen, 1% w/w nitrogen, and 1% w/w other elements (mainly calcium, potassium, sodium, magnesium, iron, and manganese) by weight. The quantity of water present has great effect on the heating value and ranges from 25 to 50% in green wood, and from 10 to 20% in air-dried wood.

The cellulose content of wood varies between species in the range of 40-50%. Some lignocellulosic materials can have more cellulose than wood. Cellulose is an organic polymer, consisting solely of units of glucose held together in a straight chain macromolecule. These glucose units are bound together by β -(1,4)-glycoside linkages which establish as the repeat unit for cellulose chains; cellulose must be hydrolyzed to glucose before fermentation to ethanol.

Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand linked D-glucose units and has the formula $(C_6H_{10}O_5)_n$.



Cellulose

The hydrolysis of cellulose (saccharification) produces its glucose monomers.

Wood cut in the spring and summer contains more water than that cut in the early part of the winter. A cord (8 feet long by 4 feet wide by 4 feet high) of hard wood, such as ash or maple, is approximately equal in heating value to one ton of bituminous coal; soft woods, such as pine and poplar, have less than half this amount. Wood burns with a long flame and makes comparatively little smoke; but its calorific intensity is low, averaging from 3,000 to 4,000 C. per kilo of air-dried wood. It is, however, easily kindled, the fire quickly reaches its maximum intensity, and a relatively small quantity of ash is formed. Wood is too expensive for industrial use, except in a few special cases, where freedom from dirt and smoke is necessary. Of other cellulose materials, shavings, sawdust, and straw are used for fuel in some places. They are bulky and difficult to handle, while their heat value, which depends on the amount of moisture they contain, is seldom more than from one-third to one-half that of good coal. Such waste matter as spent tan-bark and bagasse (crushed sugar cane), and the pulp from sugar beets is sometimes used for fuel for evaporation or for steam generation, but owing to the large amount of moisture they contain, the heat value is low.

When considering the type of wood for use as firewood, several characteristics are important. These include heat value, ease of splitting, weight per unit volume, ease of starting, amount of smoking, and coaling qualities. The moisture content of the wood, the number of knots, and pitch content affect these characteristics of the more common woods used as firewood.

All woods dried to the same moisture content contain approximately the same heat value per pound – from 8,000 to 9,500 BTU for fully dried wood and 5,500 to 8,500 BTU for air-seasoned wood. However, the heat content of any fire depends on wood density, resin, ash, and moisture. A general rule for estimating heat value of firewood is: one cord of well-seasoned hardwood (weighing approximately two tons) burned in an airtight, draft-controlled wood stove with a 55 to 65% efficiency is equivalent to approximately 175 gallons of #2 fuel oil or 225 therms of natural gas consumed in normal furnaces having 65 to 75% efficiencies.

See also: Biomass, Cellulose, Hemicellulose, Lignin, Lignocellulose, Wood.

Wood – Fuels from

Woodfuels are included in the sector of forests, woodlands, and trees and include all types of biofuels derived directly and indirectly from trees and shrubs grown on forest and non-forest lands.

The definition of forest is broad and includes land with a minimum tree crown cover of 10%. Woodfuels also include biomass derived from silvi-cultural activities (thinning, pruning, etc.) and harvesting and logging (tops, roots, branches, etc.), as well as industrial by-products derived from primary and secondary forest industries which are used as fuel. They also include woodfuels derived from forest energy plantations.

The conversion of wood into fuel goes mainly first through gasification or hydrolysis followed by downstream fermentation or a Fischer-Tropsch reactor. The most promising technology available today is the production of Fischer-Tropsch (FT) diesel through gasification. It offers high energy efficiency (approximately 50 %) and low carbon dioxide emissions (reduction of approximately 85%).

The production of ethanol is less effective, but ethanol has a high octane number and is therefore used as a petrol fuel additive to improve engine performance, typically added as E5 or E10. The use of higher concentrations blends of ethanol such as E85 is possible, but requires small changes to petrol engines.

The gasification process produces a synthesis gas consisting of mainly carbon monoxide and hydrogen. This gas may be fed into a Fischer-Tropsch (FT) reactor where chain growth takes place, producing a wide range of hydrocarbons, including gasoline and diesel.

The energy yield of this process is approximately 50%, and has been proven in pilot plants. An alternative use of the synthesis gas is to feed it to a fermentation reactor, where a modified bacteria culture digests the synthesis gas and produces ethanol as a product.

The hydrolysis step breaks down the cellulose and hemi-cellulose into fermentable sugars. The fermentation follows conventional technology, but with modifications in order to be able to ferment the C5 sugars. The energy yield of the process is approximately 36%. Pyrolysis and hydro thermal upgrading (HTU) are affected by high upgrading costs to enable use in normal automotive engines.

See also: Biomass, Biomass to Energy, Lignin, Lignocellulose, Wood.

Wood Gasification

Wood gasification is the process of heating wood in an oxygen-starved environment until volatile pyrolysis gases (carbon monoxide and hydrogen) are released from the wood. Depending on the final use of the typically low-energy wood (producer) gas (approximately 150 Btu/ft³), the gases can be mixed with air or pure oxygen for complete combustion and the heat produced transferred to a boiler for energy distribution. Otherwise, the gases can be cooled, filtered, and purified to remove tars (a major concern for any wood gasification process) and particulates and used as fuel for internal combustion engines, microturbines, and gas turbines.

See also: Gasification.

Wood – Hardwood

Hardwood is wood from dicot trees which are usually found in broad-leaved temperate and tropical forests. In temperate and boreal latitudes, they are mostly deciduous, but in the tropics and subtropics, the trees are mostly evergreen. Hardwood (which comes from angiosperm trees) contrasts with softwood (which comes from gymnosperm trees).

Hardwoods have a more complex structure than softwoods and are often much slower growing as a result. The dominant feature separating hardwoods from softwoods is the presence of pores (or vessels). The vessels may show considerable variation in size, shape of perforation plates (simple, scalariform, reticulate, foraminate), and structure of cell wall, such as spiral thickenings.

As the name suggests, the wood from these trees is generally harder than that of softwoods, but there are significant exceptions. In both groups, there is an enormous variation in actual wood hardness, with the range in density in hardwoods completely including that of softwoods; some hardwoods (such as balsa wood) are softer than most softwoods, while yew is an example of a hard softwood.

Hardwoods are employed in a large range of applications, including fuel, tools, construction, and the manufacture of charcoal. Solid hardwood joinery tends to be expensive compared to softwood. In the past, tropical hardwoods

were easily available, but the supply of some species, such as teak and mahogany, is now becoming scarce due to over-exploitation. Hardwoods may be used in a variety of objects, but are most frequently seen in furniture or musical instruments because of their density which adds to durability, appearance, and performance. Different species of hardwood lend themselves to different end uses or construction processes due to the variety of characteristics apparent in different timbers, including density, grain, pore size, growth and fiber pattern, flexibility, and ability to be steam bent.

See also: Softwood, Wood.

Wood Pellets

Pellets are normally of 10-30 mm of length at 8-12 mm of diameter. Notwithstanding the fact that they get an increasing popularity as a solid biofuel for heat and to a lesser extent for power generation, their employment in biomass-to-liquids processes. Pellets are usually produced from powder obtained from various residual biomass (woody and/or herbaceous) and waste, or sawdust. To form the pellets, the powder is usually forced through a matrix under high pressure, followed by immediate cooling for durability and stability. The main advantage of pellets over powder, sawdust, and other residual biomass is the much higher energy density, which significantly reduces transportation, storage, and handling costs per energy unit. The drawback of pellets is the lower energy efficiency compared to powder (2 processes instead of just 1). If dry raw material is used, the energy costs may reduce to that of chips – 1.5-2% of the energy content of pellets. If drying is actually necessary, the energy costs may raise up to 7-13%. Additional 10% can be spent for preliminary crushing of the raw material. With regard to the production of liquids from biomass, pelletizing can be justified only when remote biomass has to be brought to the biomass-to-liquids plant, if no other more cost-effective options are available.

See also: Biomass, Wood.

Wood Powder and Sawdust

Apart from chipping, another option to utilize various residual or waste woody materials is as powder. Wood powder represents fine shredding of woody biomass with particle size below 3 mm, usually approximately 1 mm. This is an important advantage over chips, since the smaller the particle size, the better the gasification. Conversely, the energy consumption of mills is typically much higher than that of chippers. The energy penalty grows exponentially with the reduction of the size of wood powder particles below 1 mm. Wood mills are robust and reliable systems, which can process materials of various quality (including with impurities) and particle size. When demolition wood is shredded, a removal of the metallic contaminants (with magnets) may be necessary before the material enters the mill.

Besides dedicated and energy-expensive milling of various woody materials, feedstock with similar particle size can be obtained also directly – sawdust, which is a residual material from sawmills. Similar to chips, when sawdust is left after processing fresh wood, its moisture content could be high, so pre-drying might be necessary.

See also: Biomass, Wood.

Wood – Softwood

Softwood is usually wood from gymnosperm trees such as pine trees and spruce trees which often reproduce using cones and occasionally nuts. The trees classified as softwoods have needle-like or scale-like leaves that, with a few exceptions, remain on the tree all through the year. Hence, softwood trees are sometimes called evergreens. Botanically, they are known as gymnosperms, and instead of bearing seeds from flowers, gymnosperms have exposed seeds in cones.

Within the softwood and hardwood groups, there is a considerable variation in actual wood hardness, the range of density in hardwoods completely including that of softwoods. Some hardwoods (such as balsa) are

softer than most softwoods, while the hardest hardwoods are much harder than any softwood. In short, the terms softwood and hardwood are archaic with questionable meaning and often belie the properties of the wood.

Softwoods are generally most used by the construction industry and are also used to produce paper pulp and card products. In many of these applications, there is a constant need for density and thickness monitoring and gamma-ray sensors have shown good performance in this case. Certain species of softwood are more resistant to insect attack from woodworm, as certain insects prefer damp hardwood. Softwoods which give a fast burning, cracking blaze are less dense and contain less total heating value per unit of volume.

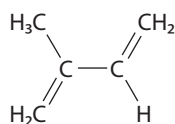
See also: Wood, Wood – Hardwood.

Wood – Solvent Extractable Material

The structure created by hydrogen bonds results in the typical material properties of the chemical constituents of wood confers insolubility in most solvents. For isolation of, for example, cellulose from wood, a direct nitration of wood yields undegraded cellulose trinitrate, which is soluble in organic solvents. On the other hand, the glycosidic linkages are easily cleaved by strong mineral acids and therefore, cellulose can be hydrolyzed to simple sugars. However, for a complete hydrolysis of cellulose, concentrated acid solutions must be used in order to bring about the necessary swelling and at least a partial destroying of the ordered regions. Furthermore, although native lignin derivatives behave as an insoluble and three-dimensional network, the isolated lignin derivatives exhibit maximum solubility in a variety of solvents including dioxane, acetone, methyl cellosolve, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide.

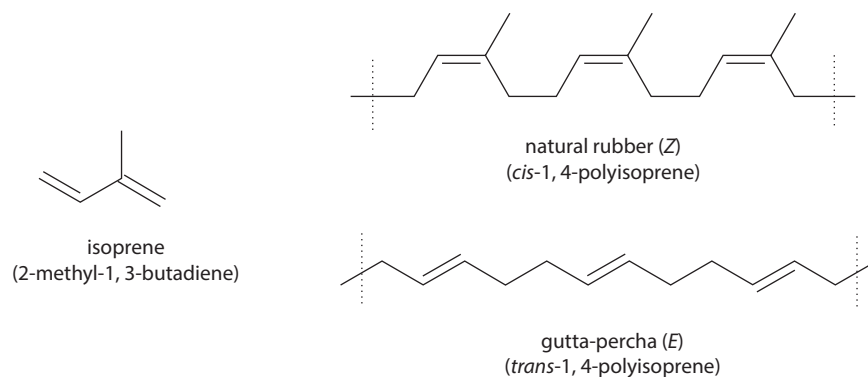
More generally, the soluble materials or extractives in wood consist of those components that are soluble in neutral organic solvents and are not only suitable for conversion to alternate fuels but can also continue and expand (if there are minimal economic constraints) the petrochemical industry. The di-chloromethane extractable content of wood is a measure of such substances such as waxes, fats, resins, phyto-sterols and non-volatile hydrocarbon derivatives. The amount of extractives is highly dependent on the seasoning or drying of wood. The ethanol-benzene extractable content of the wood consists of certain other di-chloromethane insoluble components such as low-molecular-weight carbohydrates, salts, and other water-soluble substances. Most water-soluble and volatile compounds are removed during pulping. The extractives reduce pulp yield, increase pulping and bleaching chemical consumption, and create problems such as foaming during paper-making if not removed.

For isolation of the extractives from wood, the different methods can be used. Volatile extractives are represented by high-volatile compounds which can be separated by water distillation. They are mainly composed of mono-terpene derivatives and other volatile terpene derivatives, terpenoid derivatives as well as of many different low molecular compounds. The term *terpenes* typically refers to pure hydrocarbon derivatives, whereas the compounds collectively referred to as *terpenoids* have one or more oxygen-containing functional groups, such as hydroxyl, carbonyl, and carboxylic acid groups in the molecule. The basic structural unit of terpenes is isoprene, and they can be divided into subgroups according to the number of isoprene units linked in a terpene.



Isoprene (2-methyl-1,3-butadiene)

Mono-, sesqui-, di-, tri- and polyterpenoids are the most abundant terpenes in wood. In addition to this classification, terpenes can be generally classified according to the number of rings within a structure, for example, into acyclic, monocyclic, bicyclic, tricyclic, and tetracyclic terpenes. Various polypropylene derivatives are also present in certain wood species in the form of rubber and gutta percha, and, in these macromolecules, the number of isoprene units is high.



Structure of natural rubber and gutta percha

Monoterpenes and monoterpenoids are volatile compounds and contribute substantially to the odor of wood. Monoterpenoids occur mainly in softwood oleoresin, either as hydrocarbons or their derivatives. Monoterpenes represent one of the most important constituents of the resin canal extractives and exudates of softwoods. Although monoterpenes and monoterpenoids are rare in common hardwood species, some of these compounds are minor constituents of the oleoresins of tropical hardwoods.

Sesquiterpenes and sesquiterpenoids represent a wide variety of compounds, and they are found as components of canal resin and of the heartwood deposits of softwoods. Sesquiterpenes and -terpenoids are found in many tropical hardwoods but are rare components of hardwoods from temperate zones. Since these compounds occur usually only in small amounts and are therefore commercially less important.

Diterpenes and diterpenoids constitute a major part of the canal extractives and are of great industrial importance. Diterpenoids can be divided into acyclic, bicyclic, tricyclic, tetracyclic, and macrocyclic structure types. Diterpenoids are present either as hydrocarbons or as derivatives with hydroxyl, carbonyl, or carboxyl groups. They seem to be restricted to softwood species mainly in the form of resin acids, and only some diterpenoids have been found in tropical hardwoods.

Triterpenes and triterpenoids comprise mainly oxygenated derivatives and are traditionally treated as two classes of compounds, i.e., triterpenoids and steroids. Triterpenoids can be roughly divided into three subgroups: tetracyclic lanostane, pentacyclic lupine, and pentacyclic oleanane derivatives. Steroids are similar compound groups comparing with triterpenoids, but they differ from some of tetracyclic terpenoids only by the post-cyclization loss of methyl groups in biosynthesis process from the acyclic squalene precursor. Triterpenoids and steroids occur mainly as fatty acid esters and as glycosides, but also in the free form. Triterpenoids and steroids are common in softwoods and generally in relatively small amounts. A great variety of triterpenes and steroids are also present in many hardwoods of tropical and temperate zones. In both softwood and hardwood, the most prominent compound is sitosterol, which is potential raw material for making wood-based chemicals.

Resin is the name as a collective name for the lipophilic extractives (with the exception of phenolic substances). Resin extractives can be extracted with organic solvents. Water-soluble compounds consist of various phenol derivatives, carbohydrates, glycoside derivatives, and soluble salts, which can be extracted by cold or hot water.

Resins are divided into free acids, e.g., resin acid and fatty acid, and neutral compounds (such as fats and waxes). The resin fraction is soluble in organic solvents but insoluble in water, and therefore, it can be extracted with organic solvents, such as hexane, dichloromethane, diethyl ether, acetone, or ethanol. Different non-polar and polar solvents can be selected for isolation of the certain type of extractives from wood.

The analysis of the extractive material can be made at different levels such as (i) gravimetric determination of total extractives, (ii) determination of different component groups, and (iii) analysis of individual components. Component groups in extracts can be determined by several chromatographic techniques: gas chromatography (GC), high performance liquid chromatography (HPLC), size-exclusion chromatography (SEC), supercritical fluid chromatography (SFC), and thin-layer chromatography (TLC).

See also: Biomass, Wood.

Wood – Thermal Treatment

The thermal treatment of wood can be conveniently subdivided into the following categories: (i) the conventional drying process: for evaporating most moisture at 100 to 130°C (212 to 265°F), (ii) heat treatment of lumber: for increasing the durability, mechanical dimensional stability, and water-repellent characteristics in kilns with superheated steam at 185 to 220°C (365 to 510°F), (iii) torrefaction: a thermal treatment without oxygen at 200–300°C (390 to 570°F) and low particle heating rates (<10°C/min) with a long residence time (>1 minute), and (iv) pyrolysis: a process without oxygen for thermal conversion of wood at 400 to 800°C (750 to 1,470°F).

See also: Pyrolysis, Torrefaction.

Wood – Uses

The past abundance of timber and the dispersion of the industry have worked against advances in technology for the efficient production, conversion, and use of wood products. Fortunately, and despite its relatively recent origin as a recognized field of study, wood science has had an appreciable effect on wood technology as well as science in general. The study of wood chemistry has contributed to an understanding of the principal components of wood – cellulose and lignin – and their relationship to each other.

For example, the moisture content of a living tree varies seasonally and the average values are in the range of 40 to 50% w/w of the total wood mass. The chemical constituents of dry wood species are so-called structural substances and non-structural substances. Structural substances are cellulose, hemicelluloses, and lignin. Non-structural substances are mostly low-molecular-mass compounds, such as extractives, some water-soluble organics, and inorganics (Table W-8).

Table W-8 Interrelationships of the various constituents of wood.

Feedstock	General separation	Primary products	Secondary products
Dry wood			
	High-molecular-weight materials		
		Polysaccharides	
			Cellulose
			Hemicellulose
		Lignin	
	Low-molecular-weight materials	Organic substances	
			Extractable constituents
		Inorganic substances	

In addition, softwood differs typically from hardwood with regard to the chemical composition. Furthermore, the chemistry of the hemicellulose derivatives and lignin also differs in the various types of trees. On the other hand, the cellulose, hemicelluloses, and lignin are not uniformly distributed in wood cells, and their relative mass proportions can vary widely, depending on the morphological region and age of the wood.

Early research on hydrolysis of cellulose was prompted by fuel needs in World War I, but contributed much to the knowledge of this form of chemical reaction. As an example of an early process, the Madison Process as it was described in the 1940s was developed to hydrolyze softwood species, which is particularly valuable for the production of fuels such as ethanol. The hemicellulose sugars were recovered in the form of furfural, and only one stage was required. If hardwood species are used, a two-stage process is more desirable to maximize the recovery of both the hemicellulose and cellulose. High yields of hemicellulose products can be obtained at the milder pre-hydrolysis

conditions compared to the higher temperature required to maximize glucose yields from the cellulose in the second stage.

The several acids hydrolysis processes are now being promoted to produce ethanol from wood, but they do it in different types of equipment at slightly different acid-temperature-time conditions. The stake process uses a horizontal screw reactor. The Iotech process uses a high-pressure, short-time hydrolysis followed by rapid release of pressure. The twin-screw extruder process developed by New York University uses a high-pressure, special reactor design. The plug-flow reactor under study at Dartmouth and another developed by American Can use different methods to pump the wood and acid into the reactor. The New Zealand process under license to Ultra Systems is probably a modern version of Madison Process.

After the hydrolysis of the cellulose, the processes could be identical if the same products were to be recovered. Some of the two-stage processes differ in that the residue from the first stage is delignified with a lignin solvent. This dissolves the lignin to leave only cellulose to be hydrolyzed in the second stage. The lignin is then recovered by distilling off the solvent. This is in contrast to hydrolyzing the first stage residue to solubilize the cellulose and leave the lignin.

Wood is bulky, has less than half the heat of combustion of fuel oil, and in its green state is heavy to ship. Furthermore, the cost of a wood-burning system may be three to four times that of a gas-burning installation because of fuel storage, handling, and air quality control systems. These drawbacks have kindled interest in the production of liquid and gaseous fuels from wood. Much research is devoted to improving existing technology and devising new approaches, but such fuels are still expensive compared with crude oil-based fuels.

Finally, closely related to the conversion of wood to liquid or gaseous fuel is the use of the chemical storehouse that is wood to produce a wide range of *silvichemicals*. Many processes of these types already form the basis of chemical production on a commercial scale. But the potential to use wood as a chemical feedstock is much greater than has so far been realized. Whole wood can be gasified, liquefied, or pyrolyzed in ways comparable with those used for coal to yield a wide variety of chemicals. Cellulose, as a glucose polymer, can be hydrolyzed to the glucose monomer by acid or enzymes, and the glucose then fermented to ethanol. The ethanol can be used as a fuel or as a source of other important chemicals such as ethylene or butadiene. As an alternative, the use of glucose as substrate for fermentation would make possible production of antibiotics, vitamins, and enzymes. Hemicelluloses can easily be converted to simple sugars which can be used to produce ethanol or furfural, a potential raw material for nylon or other synthetics.

Lignin can be pyrolyzed, hydrogenated, and hydrolyzed to yield phenols, which can be further processed to benzene. Once the technology and economics are feasible, future plants will manufacture a variety of these very significant chemicals from wood, now derived from crude oil or other resources.

Charcoal continues to be used as an important industrial source of energy. For example, in Brazil, some 6 million tonnes of charcoal are produced every year for use in the heavy industry, such as steel and alloy production. The industrial demand for charcoal in the last few years has led to new, more efficient, and large-scale technologies, mainly aimed at improving charcoal yield and quality. Furthermore, although fuel wood is mainly a local source of energy, there are signs of an international trade in wood fuel developing between European and North American countries.

The dynamics of wood fuel flow are complex and very site-specific. The development of sustainable wood energy systems remains one of the most critical issues to be addressed by policy makers and community planners. With society giving increasing attention to sustainability issues, in the case of wood energy in both developing and developed countries, economic, environmental, and social issues deserve particular attention.

Woodall-Duckham Process

The Woodall-Duckham process employs a gasifier which is a vertical cylindrical vessel having a rotating grate in the bottom for ash removal. There are three functional zones within the reactor, and these are (i) a water-jacketed gasification zone, (ii) a refractory-lined distillation zone, and (iii) a refractory-lined drying zone.

Upon entering the gasifier, which operates at atmospheric pressure, the coal (0.25 to 1.5 inch) is contacted with upward flowing hot gases from the gasification zone and any moisture present in the coal is driven off by the hot

(120°C; 250°F) gases. The coal then falls into the distillation zone where the volatile matter present is driven off by the ascending hot gas, but since a relatively slow heating rate prevails, negligible cracking of the tar and oil occurs.

The devolatilized char (from noncaking coals) or semicoke (from caking coals) is further heated by the hot gases until the material passes into the gasification zone, where it is contacted countercurrently with steam and oxygen (or air) in a fixed bed whereupon the remaining carbon is mostly gasified. The temperature in the gasification zone may depend on the type of coal being processed but is usually of the order of 1,205°C (2,200°F). In the lower portions of this zone, the descending ash is contacted with incoming steam and air, thereby effecting gas preheating and ash cooling. The ash is removed from the gasifier through a rotating grate, which also serves to distribute the air and steam evenly over the entire cross section of the gasifier.

The product gas from the gasifier is withdrawn at two points in the vessel; the gas withdrawn between the distillation and drying zones is known as clear gas, whereas the gas withdrawn near the top of the vessel is called top gas. Varying the portion of gas withdrawn through the lower tap affords a means of control of the temperature of the distillation zone. As the flow of clear gas is reduced, more hot gas is forced through the distillation zone, thus increasing the temperature.

See also: Gasification, Gasifiers.

Wood Gas

Wood can be used to make both liquid and gaseous fuels. When wood is heated in the absence of air, or with a reduced air supply, it is possible to produce a liquid fuel which can be used in a similar way to conventional oil fuels. It can be used to run internal combustion engines in vehicles or generators. The gas produced from wood is a mixture of hydrogen and carbon monoxide which is similar to the coal gas which was made before the arrival of natural gas from the North Sea. This wood gas can be used in internal combustion engines or in gas turbines which can be used to power generators.

Gasification of wood has the potential for providing all fuel needs for small oil- or gas-fired boilers and supplemental fuel for large boilers. The gasification is carried out at elevated temperatures (500 to 1,500°C, 930 to 2,730°F) and at atmospheric or elevated pressures. The process involves conversion of biomass, which is carried out in the absence of air or with less air than the stoichiometric requirement of air for complete combustion. Partial combustion produces carbon monoxide as well as hydrogen which are both combustible gases. The producer gas can serve in different ways: it can be burned directly to produce heat or used as a fuel for gas engines and gas turbines to generate electricity; in addition, it can also be used as a feedstock (synthesis gas) in the production of chemicals, e.g., methanol.

See also: Wood.

Wood Smoke

Wood smoke forms when wood is made up of a complex mixture of gases and fine particles (particulate matter, PM). In addition to particle pollution, wood smoke contains several toxic harmful air pollutants including benzene, formaldehyde, acrolein, and polycyclic aromatic hydrocarbon derivatives (PAHs, also known as polynuclear aromatic hydrocarbon derivatives, PNAs).

Wood smoke is by far the most compelling argument against wood heating. In cold climates, a frigid, stagnant air mass traps the smoke close to the ground. In the process of wood combustion, wood vaporizes when heated into gases and tar particles. If the temperature is high enough, the tar particles vaporize into chemicals and carbon particles. If the temperature is higher still and there is oxygen present, the gases and particles burn in bright flames.

Chemically, wood is approximately 50% w/w carbon and the rest is mostly made up of oxygen and hydrogen. When a piece of wood is heated, it starts to smoke and turn black at the same time. This is because the other products vaporize under intense heat faster than the carbon burns, so smoking leaves much of the carbon behind until only charcoal remains. The smoke that vaporizes out of the wood is a cloud of nasty, gooey little droplets of a tar-like liquid. Chemically, these droplets are actually big, gooey, complicated hydrocarbon molecules that take a number of different forms, mostly bad.

When wood is burned correctly in a bright, hot, turbulent fire, what is observed is the tar droplets rising off the wood into a zone of extreme heat where they re-vaporize, undergoing thermal decomposition into (for the most part) gaseous constituents. This leaves carbon dioxide, some carbon monoxide and a number of other gases, water vapor and some not quite completely oxidized hydrocarbon products (typically identified as particulate emissions).

The sentiment that wood smoke, being a natural substance, must be benign to humans is still sometimes heard. It is now well established, however, that wood-burning stoves and fireplaces as well as wild fires and agricultural fires emit significant quantities of known health-damaging pollutants, including several carcinogenic compounds (Naeher *et al.*, 2007). Two of the principal gaseous pollutants in wood smoke, carbon monoxide (CO) and the oxides of nitrogen (NO_x), add to the atmospheric levels of these regulated gases emitted by other combustion sources. Thus, there are two issues related to wood smoke and they are (i) whether or not woodsmoke should be regulated and/or managed separately, even though some of the individual constituents are already regulated in many jurisdictions and (ii) whether or not woodsmoke particles pose different levels of risk than other ambient particles of similar size.

The particulate matter wood smoke is extremely small and therefore is not filtered out by the nose or the upper respiratory system. Instead, these small particles end up deep in the lungs where they remain for months, causing structural damage and chemical changes. The carcinogenic chemicals in wood smoke adhere to these tiny particles, which enter deep into the lungs.

See also: Volatile Organic Compounds.

Woody Feedstock

A woody (wood-based) feedstock having properties such as (i) a particle size that is too large, (ii) a particle size that is mixed or a too dissimilar particle size, and (iii) a high content of impurities such as water, leads to a difficult gasification process. Hence, woody biomass (Table W-7) normally undergoes preliminary treatments and transformations into feedstocks, which are more suitable for gasification and further processing. Such feedstocks could be wood chips, sawdust, wood powder, or pellets.

See also: Wood, Wood Biomass.

Xylan

Xylan (Figure X-1) is a polymer of xylose with a repeating unit of $C_5H_8O_4$, found in the hemicellulose fraction of biomass and can be hydrolyzed to xylose. The xylan derivatives are composed of β -1,4-linked xylose (a pentose sugar) residues with side branches of α -arabino-furanose and α -glucuronic acids and contribute to cross-linking of cellulose microfibrils and lignin through ferulic acid residues. On the basis of substituted groups, xylan can be categorized into three classes: (i) glucuronoxylan, (ii) neutral arabinoxylan, and (iii) glucuronoarabinoxylan.

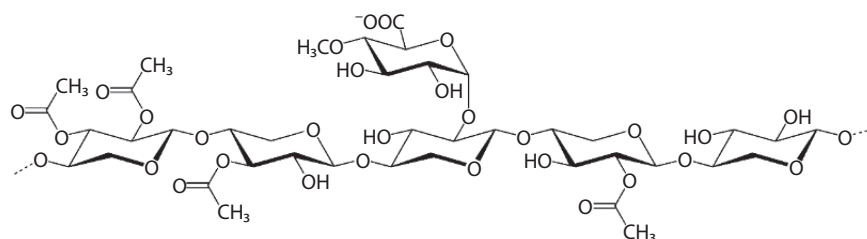


Figure X-1 Structure of xylan from hardwood

The variation in structure of the glucan derivatives and the xylan derivatives is due to differences in the amounts of the main chemical constituents of biomass (cellulose, hemicelluloses, and lignin, all of which have different uses) being present in different proportions in the various parts of the plant.

In terms of xylan content, genetics as well as environmental factors affect the chemical composition of the various parts of the plant, and it was found that husk, followed by rind and pith, has the highest sugar (glucan + xylan) content. The term glucan represents diverse glucose polymers that differ in the position of glycosidic bonds, which can be short or long, branched or unbranched, alpha or beta isomers, and soluble or insoluble. On the other hand, the term represents a group of hemicellulose derivatives.

Xylene

Xylene (sometimes referred to as xylol) refers to a mixture of three aromatic hydrocarbon isomers ($CH_3C_6H_4CH_3$) (Figure X-2) which is used as a solvent in the printing, rubber, and leather industries.

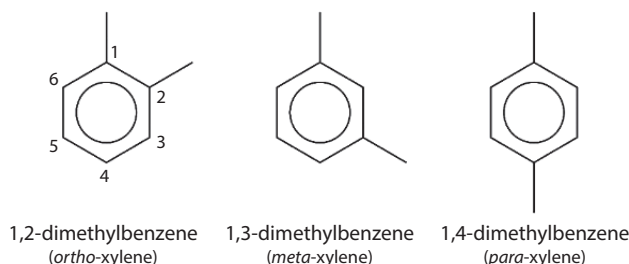


Figure X-2 The three isomers of xylene.

Xylene is a clear, colorless, sweet-smelling liquid that is highly flammable. It is usually refined from crude oil. The chemical and physical properties of xylene differ according to the respective isomers (Table X-1). Xylene is also used as an inhalant drug for its intoxicating properties.

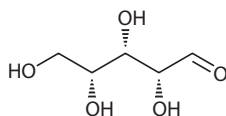
Table X-1 The general properties of the xylene isomers.

Common name	Xylene	o-Xylene	m-Xylene	p-Xylene
Systematic name	Dimethylbenzene	1,2-Dimethylbenzene	1,3-Dimethylbenzene	1, 4-Dimethylbenzene
Other names	<i>Xylol</i>	<i>o</i> -Xylol; Ortho-xylene	<i>m</i> -Xylol; Meta-xylene	<i>p</i> -Xylol; Para-xylene
Molecular formula	C_8H_{10}			
Molar mass	106.16 g/mol			
Appearance	Clear, colorless liquid			
Density (phase)	0.864 g/mL (liquid)	0.88 g/mL (liquid)	0.86 g/mL (liquid)	0.86 g/mL (liquid)
Solubility (water)	Practically insoluble			
	Soluble in non-polar solvents such as aromatic hydrocarbons			
Melting point	-47.4°C (-53.3°F)	-25°C (-13°F)	-48°C (-54°F)	13°C (55°F)
Boiling point	138.5°C (281.3°F)	144°C (291°F)	139°C (282°F)	138°C (280°F)
Flash point		17°C (63°F)	25°C (77°F)	25°C (77°F)
Viscosity		0.812 cP @ 20°C	0.62 cP @ 20°C	0.34 cP @ 30°C

See also: Petrochemicals.

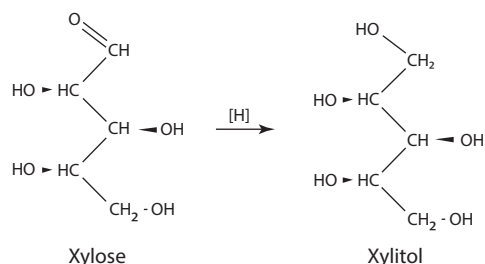
Xylose

Xylose (Figure X-3) is a hydrolysis product of xylan, which is the main part of hemicellulose present in all flora, particularly in birch and reed.

**Figure X-3** Simple formula for xylose.

Xylitol has become a popular sweetening agent, particularly because of its anti-carries properties. Xylitol is obtained by catalytic hydrogenation of xylose. Hydrogenation of xylose is industrially carried out in three-phase (semi)batch reactors over suspended Raney nickel catalyst. The traditional approach is based on the analysis of the main components only, although it is known that xylulose, arabinitol, furfural, and xylonic acid can appear as by-products. In order to optimize the reaction conditions of an industrial hydrogenation process, it is, however, necessary to have a kinetic model for the formation of both the main and by-products.

Xylose is reduced on a variety of metal catalysts based on nickel to xylitol. Xylose was hydrogenated into xylitol (Figure X-4), a polyol that is widely employed as food, cosmetic, and pharmaceutical additives.

**Figure X-4** Reduction of xylose.

Xylose Fermentation

The pentose (C5) sugar D-xylose (Figure X-5) comprises approximately 30 to 60% w/w of the total fermentable carbohydrate sugars in hardwood and herbaceous biomass and affords a feedstock for the production of ethanol by fermentation.

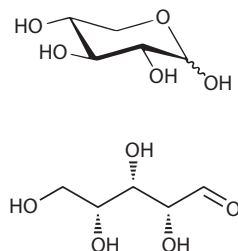
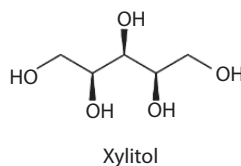


Figure X-5 Alternate representations of xylose.

The dextrorotary form of xylose, D-xylose, refers usually to the endogenously occurring form of the sugar in living things.

Microorganisms that rapidly ferment xylose to ethanol at high yields are essential to the development of cost-effective, large-scale xylose to ethanol processes. The ability of certain fungi and bacteria to ferment xylose to ethanol has been recognized for many years. Also, the reduction of xylose by catalytic hydrogenation produces the common food additive sweetener substitute xylitol which is a chemical compound with the formula $C_5H_{12}O_5$ [$HO(CH_2)(CHOH)_3CH_2OH$] and is a colorless or white crystalline solid that is soluble in water.



The efficient fermentation of xylose and other hemicellulose constituents is essential for the development of an economically viable process to produce ethanol from biomass. Xylose fermentation using pentose yeasts has proven to be difficult due to the requirement for oxygen during ethanol production, the acetate toxicity, and the production of xylitol as a by-product.

See: Fermentation.

Yeast

Yeasts are eukaryotic heterotrophic organisms (organisms whose cells have a nucleus enclosed within a nuclear envelope) belonging to fungi. In contrast to other eukaryotes, yeasts possess thick and rigid cell wall. Yeast is also considered as the oldest domesticated organism used for thousands of years for the production of alcoholic beverages and raised bread. As a source of carbon and energy, yeasts are capable of fermenting carbohydrates to, for example, bioethanol.

The use of the yeast in food industry as baker's yeast, fodder yeast, for the beer, wine, and spirit production is of great importance. Modern biotechnologies use yeast for the production of various substances (vitamins, enzymes, antibiotics, amino acids, proteins). It can be genetically modified to gain new and more convenient properties and to produce desired compounds. Being relatively easy to handle (mutant isolation, gene transfer, cultivation) and of known genome, yeast is a suitable model organism for the study of physiological and metabolic processes and genetics of eukaryotes. However, some of the yeast genera belong to pathogens that are hazardous for immunocompromised people.

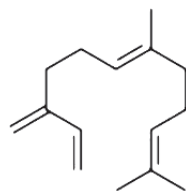
Yeast can, to a lesser extent, ferment oligosaccharides and polysaccharides. Glycerol, lactic acid, ethanol, methanol, and alkane derivatives can also serve as sources of carbon. The sources of carbon and energy are in most yeasts converted aerobically by glycolysis and citric acid cycle. However, in yeast with predominantly fermentative metabolism, the energy is formed during the fermentation process.

Yeast is one of the most widely used industrial microorganisms worldwide. It is irreplaceable in food and pharmaceutical industry and in some research, technical, and medical areas. Production of biologically active compounds of yeast, its biodegradation activity, and production of food and fodder biomass is also of great importance. In addition to the traditional technologies, yeast finds an ever-increasing application in a number of other fields (such as in the production of organic acids and vitamins). Genetically modified yeast can produce pharmacological formulas for both prevention and treatment.

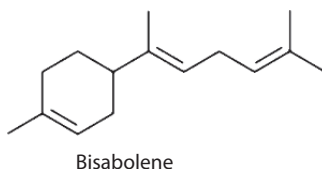
Bioethanol has been identified as the mostly used biofuel worldwide since it significantly contributes to the reduction of crude oil consumption and environmental pollution. It can be produced from various types of feedstocks such as sucrose, starch, lignocellulosic, and algal biomass through fermentation process by microorganisms. Compared to other types of microorganisms, yeast is the common microbes employed in ethanol production due to its high ethanol productivity, high ethanol tolerance, and ability of fermenting a wide range of sugars. However, there are some challenges in yeast fermentation which inhibit ethanol production such as high temperature, high ethanol concentration, and the ability to ferment pentose (C5) sugars.

Various types of yeast strains have been used in fermentation for ethanol production including hybrid, recombinant, and wild-type yeasts. Yeasts can directly ferment simple sugar derivatives into ethanol, while other type of feedstocks must be converted to fermentable sugars before it can be fermented to ethanol. The common processes involved in ethanol production are pretreatment, hydrolysis, and fermentation. Production of bioethanol during fermentation depends on several factors such as temperature, sugar concentration, pH, fermentation time, agitation rate, and inoculum size. The efficiency and productivity of ethanol can be enhanced by immobilizing the yeast cells.

In addition, yeast can be turned into a producer of higher-molecular-weight alcohol derivatives (such as 1-butanol and iso-butanol), sesquiterpene derivatives (such as farnesene and bisabolene), and fatty acid ethyl esters (biodiesel).



Farnesene



See also: Fermentation, Fermentation Chemistry, Hydrolysis and Fermentation of Sugar

Yellow Cake

Yellow cake (yellowcake, sometimes referred to as also called urania, which is uranium oxide UO_2) is a type of uranium concentrate powder obtained from the solution of a leaching process in an intermediate step in the processing of uranium ore. The production of the yellow cake is a step in the processing of uranium after it has been mined but before fuel fabrication or the uranium enrichment process. Yellow cake concentrates are prepared by various extraction and refining methods, depending on the types of ores. Typically, yellow cake is obtained through the milling and chemical processing of uranium ore, forming a coarse powder that has a pungent odor, is insoluble in water, and contains about 80% uranium oxide, which melts at approximately $2,880^\circ\text{C}$ ($5,215^\circ\text{F}$).

In the process to produce yellow cake, the raw uranium ore is crushed to a fine powder to produce pulped ore which is further processed with concentrated acid, alkaline, or peroxide solutions to leach out the uranium. After drying and filtering, the product is yellow cake.

Yellow cake is used in the preparation of uranium fuel for use in a nuclear reactor for which it is smelted into purified uranium oxide (UO_2) to be used in fuel rods for use in a pressurized heavy water reactor as well as in other systems that use natural non-enriched uranium.

Purified uranium can also be enriched to uranium-235 (U-235 , ^{235}U) by a process in which the uranium oxides are combined with fluorine to form uranium hexafluoride (UF_6) after which isotope separation is carried out by the process of gaseous diffusion or in a gas centrifuge. The result is a low-enriched uranium is can produce that contains up to 20% w/w ^{235}U that is suitable for use in most large civilian electric-power reactors. With further processing, highly enriched uranium is obtained which contains 20% w/w or more ^{235}U that is suitable for use in compact nuclear reactors – that is typically used to power naval warships and submarines. Further processing can yield weapons-grade uranium (which typically has levels of ^{235}U levels above 90%, which is suitable for use in nuclear weapons).

See also: Nuclear Energy, Uranium.

Yellow Flax

The yellow flax (or golden flax, *Linum flavum*) is a species of flowering plant in the family Linaceae that is native to central and southern Europe. It is an erect, woody perennial that grows up to approximately 12 inches tall by 8 inches broad with dark green, with semi-evergreen leaves, and terminal clusters of bright yellow, five-petalled flowers in the Spring.

The oil contains omega-3 fatty acids and has been shown to have several health benefits, such as reduced blood pressure and improved regularity as well as a source of liquid fuels, such as biodiesel.

See: Flax and Flaxseed Oil, Linseed Oil.

Yellow Grease

Yellow grease (sometimes referred to as used vegetable oil or waste vegetable oil) is a term from the rendering industry – usually means used frying oils from deep fryers and restaurants' grease traps; can also refer to lower-quality grades of tallow from rendering plants. Yellow grease contains spent cooking oils derived from industrial- or

commercial-scale cooking operations. Thus, yellow grease is used cooking oil whose quality has degraded due to the oxidation, polymerization, or hydrolysis process.

Yellow grease is used cooking oil whose quality has degraded due to the oxidation, polymerization, or hydrolysis process. In previous studies, yellow grease refining had been conducted either by adsorption or by using membrane technology. However, adsorption is a method that is commonly used in refining yellow grease and is the process of choice because the process is easy to perform, and usually is effective in reducing free fatty acid in yellow grease.

See also: Waste Vegetable Oil.

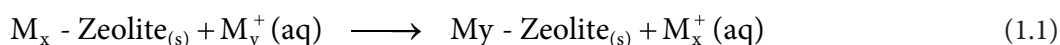
Zeolite

A zeolite is a crystalline aluminosilicate used as a catalyst and having a particular chemical and physical structure.

Zeolites provide the cracking function in many hydrocracking catalysts, as they do in fluid catalytic cracking catalysts. The zeolites are crystalline aluminosilicates, and in almost all commercial catalysts today, the zeolite used is faujasite. Pentasil zeolites, including silicalite and ZSM-5, are also used in some catalysts for their ability to crack long chain paraffins selectively. Typical levels are 25 to 50% w/w zeolite in the catalysts, with the remainder being the hydrogenation component and a silica (SiO_2) or alumina (Al_2O_3) binder. The exact recipes are guarded as trade secrets.

Typical naturally occurring zeolites include *analcite* (also called *analcime*) $\text{Na}(\text{AlSi}_2\text{O}_6)$, and *faujasite* $\text{Na}_2\text{Ca}(\text{AlO}_2)_2(\text{SiO}_2)_4 \cdot \text{H}_2\text{O}$ that is the structural analog of the synthetic *zeolite X* and *zeolite Y*. *Sodalite* $(\text{Na}_8[(\text{Al}_2\text{O}_2)_6(\text{SiO}_2)_6]\text{Cl}_2)$ contains the truncated octahedral structural unit known as the *sodalite cage* that is found in several zeolites. The corners of the faces of the cage are defined by either four or six Al/Si atoms, which are joined together through oxygen atoms. The zeolite-structure is generated by joining *sodalite* cages through the four-Si/Al rings, so enclosing a cavity or *super cage* bounded by a cube of eight *sodalite* cages and readily accessible through the faces of that cube (*channels* or *pores*). Joining *sodalite* cages together through the six-Si/Al faces generates the structural frameworks of faujasite, zeolite X, and zeolite Y. In zeolites, the effective width of the pores is usually controlled by the nature of the cation (M^+ or M^{2+}).

Zeolite catalysts can vary in their framework: isomorphous substitution, cation exchange, impregnation, and intercalation. The silicon-to-aluminum ratio (Si/Al ratio) represents the amount of isomorphous substitution in an aluminosilicate zeolite, with a typical range of 1-5. The Si/Al ratio varies, depending on the zeolite. ZSM-5, for example, has a high Si/Al ratio (10-100), while the lowest or the minimum Si/Al ratio possible for an aluminosilicate zeolite is 1. Lowenstein's rule states that there can be no Al-O-Al tetrahedron linkages in the frameworks of zeolites. Zeolites with the faujasite structure, i.e., X and Y, demonstrate Lowenstein's rule: zeolite Y has a Si/Al ratio greater than 1.5, whereas zeolite X has a Si/Al ratio in the range 1-1.5.



Cation-exchange treatment is therefore usually repeated several times using a fresh solution of the cations for exchange in order to achieve a complete exchange. The process of cation-exchange is reversible and is dependent on the concentration of cations in the solution, catalyst proportions, and the zeolite itself. Complete ion-exchange is possible using a simple apparatus.

Zeolite catalysts are mostly used as solid acids or as solid support species for reactions involving transformations of hydrocarbons. The acidity of zeolites (active Brønsted sites, as proton donors) can be increased by cation-exchange within the zeolite channels using ammonium ions and then calcination (Equations 1.2 and 1.3) or using certain polyvalent cations.



The solid becomes highly acidic after an ammonium exchanged zeolite is heated to remove ammonia (NH_3). The protons are mobile between the anionic sites at high temperature (approximately 200°C , 390°F). At even higher temperature (approximately 500°C , 930°F), the removal of water (as vapor) from the solid leads to Lewis acid site

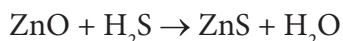
formation (characterized as electron pair acceptor). The formation of such Lewis acid sites enables the catalyst to become more efficient for reactions involving Lewis acid catalysis.

The geometric characteristics of the zeolites are responsible for their special properties, which are particularly attractive to the refining industry. Specific zeolite catalysts have shown up to 10,000 times more activity than the so-called conventional catalysts in specific cracking tests. The mordenite-type catalysts are particularly worthy of mention since they have shown up to 200 times greater activity for hexane cracking in the temperature range 360 to 400°C (680 to 750°F).

Other zeolite catalysts have also shown remarkable adaptability to the refining industry. The resistance to deactivation of the type Y zeolite catalysts containing either noble or non-noble metals is remarkable, and a catalyst life of up to 7 years has been obtained commercially in processing heavy gas oils in the Unicracking-JHC processes. The operating life depends on the nature of the feedstock, the severity of the operation, and the nature and extent of operational upsets. Gradual catalyst deactivation in commercial use is counteracted by incrementally raising the operating temperature to maintain the required conversion per pass. The more active a catalyst, the lower the temperature required. When processing for gasoline, lower operating temperatures have the additional advantage that less of the feedstock is converted to *iso*-butane.

Zinc Oxide Process

Zinc oxide is also used for hydrogen sulfide removal from the gas stream. The zinc oxide media particles are extruded cylinders 3–4 mm in diameter and 4–8 mm in length. This uniform sizing allows for relatively accurate pressure drop calculations in designing reactors. The general reaction of zinc oxide with hydrogen sulfide is:



At increased temperatures 205 to 370°C (400 to 700°F), zinc oxide has a rapid reaction rate, therefore providing a short mass transfer zone, resulting in a short length of unused bed and improved efficiency. At operating temperatures, the zinc oxide sorbent has a maximum sulfur loading of 0.3 to 0.4 kg sulfur/kg sorbent. In large industrial plants, this process achieves a high degree of efficiency, as the spent zinc oxide bed can be used for metal and sulfur recovery.

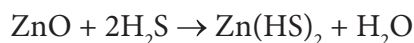
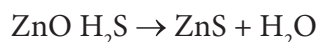
Generally, the iron oxide process is suitable only for small-to-moderate quantities of hydrogen sulfide. Approximately 90% v/v of the hydrogen sulfide can be removed per bed, but bed clogging by elemental sulfur occurs and the bed must be discarded, and the use of several beds in series is not usually economical. The removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the Ferrox process or the Stretford process. The *Ferrox process* is based on the same chemistry as the iron oxide process except that it is fluid and continuous.

The Stretford process employs a solution containing vanadium salts and anthraquinone disulfonic acid.

See Gas Cleaning.

Zinc Oxide Slurry Process

The zinc oxide slurry process consists of a simple vertical bubble contactor with the gas providing sufficient agitation to keep zinc oxide particles in suspension in addition to a dispersant:



The majority of the hydrogen sulfide is converted to zinc sulfide. However, zinc mercaptide is a minor product and will form sludge in the reactor which can contribute to foaming.

The Chemsweet process uses zinc acetate, dispersants, and antifoam additives to stabilize the process. The addition of zinc acetate establishes a more controlled reaction. Zinc acetate dissolves to equilibrium to produce zinc ions, which then react with H_2S yielding zinc sulfide and acetic acid. The addition of acetic acid causes more zinc to dissociate, thereby controlling the concentration of zinc ions in solution. While a zinc slurry plant can be easy to operate and install, the high cost of the reactant and difficulty of disposing zinc sulfide wastes make it less attractive. The spent media can be disposed of in an industrial landfill only after passing leachate tests. If the leachate contains more than 20 ppm of zinc and zinc compounds, then it must be treated as a hazardous waste.

Conversion Factors

1. Length Conversions

1 inch = 25.4 mm

1 foot = 0.3048 meter

1 yard = 0.9111 meter

1 mile = 1.609 kilometer

2. Concentration Conversions

1 part per million (1 ppm) = 1 microgram per liter (1 $\mu\text{g/L}$)

1 microgram per liter (1 $\mu\text{g/L}$) = 1 milligram per kilogram (1 mg/kg)

1 microgram per liter ($\mu\text{g/L}$) $\times 6.243 \times 10^8 = 1$ lb per cubic foot (1 lb/ft³)

1 microgram per liter (1 $\mu\text{g/L}$) $\times 10^{-3} = 1$ milligram per liter (1 mg/L)

1 milligram per liter (1 mg/L) $\times 6.243 \times 10^5 = 1$ pound per cubic foot (1 lb/ft³)

1 gram mole per cubic meter (1 g mol/m³) $\times 6.243 \times 10^5 = 1$ pound per cubic foot (1 lb/ft³)

10,000 ppm = 1% w/w

1 ppm hydrocarbon in soil $\times 0.002 = 1$ lb of hydrocarbons per ton of contaminated soil

3. Density

1 pound per cubic foot = 16.03 kilograms per cubic meter

4. Weight Conversion

1 ounce (1 oz) = 28.3495 grams (28.3495 g)

1 pound (1 lb) = 0.454 kilogram

1 pound (1 lb) = 454 grams (454 g)

1 kilogram (1 kg) = 2.20462 pounds (2.20462 lb)

1 stone (English, 1 st) = 14 pounds (14 lb)

1 ton (US; 1 short ton) = 2,000 lbs

1 ton (English; 1 long ton) = 2,240 lbs

1 metric ton = 2204.62262 pounds

1 tonne = 2204.62262 pounds

5. Temperature Conversions

$^{\circ}\text{F} = (^{\circ}\text{C} \times 1.8) + 32$

$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$

$(^{\circ}\text{F} - 32) \times 0.555 = ^{\circ}\text{C}$

Absolute zero = -273.15°C

Absolute zero = -459.67°F

6. Area

1 square centimeter (1 cm²) = 0.1550 square inches

1 square meter (1 m²) = 1.1960 square yards

1 square kilometer (1 km²) = 0.3861 square miles

1 square inch (1 inch²) = 6.4516 square centimeters = 645.2 square millimeters

1 square foot (1 ft²) = 0.0929 square meters

1 square yard (1 yd^2) = 0.8361 square meters
 1 acre = 4046.9 square meters
 1 hectare = 2.4711 acres
 1 square mile (1 mi^2) = 2.59 square kilometers

7. Volume Conversions

1 cubic inch = 16.39 cubic centimeters
 1 cubic foot = 0.028 cubic meters = 28.32 liters
 1 cubic yard = 0.7646 cubic meters = 764.6 liters
 1 UK gallon = 1 Imperial gallon = 4.546 liters
 1 US gallon = 3.785 liters

8. Nutrient Conversion Factor

1 pound phosphorus $\times 2.3$ ($1 \text{ lb P} \times 2.3$) = 1 pound phosphorous pentoxide ($1 \text{ lb P}_2\text{O}_5$)
 1 pound potassium $\times 1.2$ ($1 \text{ lb K} \times 1.2$) = 1 pound potassium oxide ($1 \text{ lb K}_2\text{O}$)

9. Sludge Conversions

1,700 lbs wet sludge = 1 yd^3 wet sludge
 1 yd^3 sludge = wet tons/0.85
 Wet tons sludge $\times 240$ = gallons sludge
 $1 \text{ wet ton sludge} \times \% \text{ dry solids}/100 = 1 \text{ dry ton of sludge}$

10. Other Conversions

14.7 pounds per square inch (14.7 psi) = 1 atmosphere (1 atm)
 $1 \text{ kilopascal (kPa)} \times 9.8692 \times 10^{-3} = 14.7 \text{ pounds per square inch (14.7 psi)}$
 $1 \text{ yd}^3 = 27 \text{ ft}^3$
 1 US gallon of water = 8.34 lbs
 1 Imperial gallon of water = 10 lbs
 $1 \text{ yd}^3 = 0.765 \text{ m}^3$
 1 acre-inch of liquid = 27,150 gallons = 3.630 ft^3
 $1 \text{ ft depth in 1 acre (in-situ)} = 1,613 \times (20 \text{ to } 25 \% \text{ excavation factor}) = \sim 2,000 \text{ yd}^3$
 1 yd^3 (clayey soils-excavated) = 1.1 to 1.2 tons (US)
 1 yd^3 (sandy soils-excavated) = 1.2 to 1.3 tons (US)

Further Reading

- Accettola, F., Guebitz, G.M. and Schoeftner, R. 2008. Siloxane Removal from Biogas by Biofiltration: Biodegradation Studies. *Clean Technol. Environ. Policy*, 10(2): 211-218.
- Ajhar, M., Travesset, M., Yüce, S. and Melin, T. 2010. Siloxane Removal from Landfill and Digester Gas – A Technology Overview. *Bioresour. Technol.*, 101(9): 2913-2923.
- ASTM International. 2020. Annual Book of Standards. ASTM International, West Conshocken, Pennsylvania.
- Attfield, R. 1983. *The Ethics of Environmental Concern*. Blackwell Books, Oxford, United Kingdom.
- Balat, M. 2011. Fuels from Biomass. In: *The Biofuels Handbook Part 1*, Chapter 3. The Royal Society of Chemistry, Cambridge, United Kingdom.
- Bettencourt, J.A. 2004. *Fundamentals of Plasma Physics Third Edition*. Springer Science, New York.
- Bommarius, A.S., Riebel, B.R. 2004. *Biocatalysis: Fundamentals and Applications*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.
- Carson, P., and Mumford, C. 2002. *Hazardous Chemicals Handbook 2nd Edition*. Butterworth-Heinemann, Elsevier Science, Oxford, United Kingdom.
- CEA. 2016. *Nuclear Reactors – From Fission to Power Generation*. Education Booklet No. 6. Commissariat à l’Energie Atomique et aux Energies Alternatives (Commission for Atomic Energy and Alternative Energy). Direction de la Communication, Paris, France.
- Chadeesingh, R. The Fischer-Tropsch Process. In *The Biofuels Handbook*. J.G. Speight (Editor). The Royal Society of Chemistry, London, United Kingdom. 2011. Part 3, Chapter 5, Page 476-517.
- Chesworth, W. (Editor). 2008. *Encyclopedia of Soil Science*. Springer, Dordrecht, Netherlands.
- Christopherson, R.W., 2008. *Geosystems: An Introduction to Physical Geography 7th Edition*. Pearson Prentice-Hall, New York.
- Davis, B.H., and Ocelli, M.L. 2010. *Advances in Fischer-Tropsch Synthesis, Catalysts, and Catalysis*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Demirbaş, A. 2009. *Biofuels: Securing the Planet’s Future Energy Needs*. Springer Verlag, London, United Kingdom.
- Demirbaş, A. 2010. *Biorefineries: For Biomass Upgrading Facilities*. Springer-Verlag, London, United Kingdom.
- Easterbrook, G. 1995. *A Moment on the Earth: The Coming Age of Environmental Optimism*. Viking Press, New York.
- El-Gendy, N.S., and Speight, J.G. 2016. *Handbook of Refinery Desulfurization*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Foster, R., Ghassemi, M., and Cota, A. 2010. *Solar Energy: Renewable Energy and the Environment*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Freidberg, J.P. *Plasma Physics and Fusion Energy*. Cambridge University Press, Cambridge, United Kingdom.
- Gislon, P., Galli, S. and Monteleone, G. 2013. Siloxanes Removal from Biogas by High Surface Area Adsorbents. *Waste Manag.*, 33(12): 2687-2693.
- Gomez, E., Rani, D.A., Cheeseman, C.R., Deegan, D., Wise, M., and Boccaccini, A.R. 2009. Thermal Plasma Technology for the Treatment of Wastes: A critical Review. *Journal of Hazardous Materials*, 161(2-3): 614-626.
- Gore, A 1993. *Earth in the Balance: Ecology and the Human Spirit*. Penguin Books USA Inc., New York.
- Gulliver, J.S., and Arndt, R.E.A. (Editors). 1991. *Hydropower Engineering Handbook*. McGraw-Hill Inc., New York.
- Haas, R., Mez, L., and Ajanovic, A. (Editors). 2019. *The Technological and Economic Future of Nuclear Power*. Springer VS, Vienna, Austria, <https://link.springer.com/book/10.1007/978-3-658-25987-7>
- International Atomic Energy Agency. 2017. *Industrial Applications of Nuclear Energy*. Report No. NP-T-4.3. International Atomic Energy Agency, Vienna, Austria. :
- Jazib, J. 2018. *Basics of Environmental Sciences*. Iqra Publishers, New Delhi, India.
- Knief, R.A. 1992. *Nuclear Engineering: Theory and Technology of Commercial Nuclear Power*. Taylor & Francis, Washington, D.C.
- Krech, S., McNeill, J.R., and Merchant, C. 2003. *Encyclopedia of World Environmental History*. Volume 1-3. Routledge, Taylor & Francis Group, London, United Kingdom.

- Lago, C., Caldés, N., and Lechón, Y. 2019. *The Role of Bioenergy in the Emerging Bioeconomy: Resources, Technologies, Sustainability and Policy*. Elsevier BV, Amsterdam, Netherlands.
- Lee, S., Speight, J.G., and Loyalka, S.K. 2007. *Handbook of Alternative Fuel Technologies*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Lee, S., and Shah, Y.T. 2013. *Biofuels and Bioenergy: Processes and Technologies*. CRC Press, Taylor & Francis Group, Boca Raton Florida.
- Luciani, G. 2013. *Security of Oil Supplies: Issues and Remarks*. Claeys & Casteels, Deventer, Netherlands.
- Luque, R., and Speight, J.G. (Editors). 2015. *Gasification for Synthetic Fuel Production: Fundamentals, Processes, and Applications*. Woodhead Publishing, Elsevier, Cambridge, United Kingdom.
- Manwell, J.F., McGowan, J.G., and Rogers, A.L. 2009. *Wind Energy Explained: Theory, Design and Application Second Edition*. John Wiley & Sons inc., Hoboken, New Jersey.
- McCabe, W.L., Smith, J.C., and Harriot, P. 2005. *Unit Operations of Chemical Engineering 7th Edition*. McGraw-Hill, New York.
- McCracken, G., and Stott, P. 2005. *Fusion – The Energy of the Universe*. Elsevier Academic Press, Burlington, Massachusetts.
- Nersesian, R.L. 2007. *Energy for the 21st Century: A Comprehensive Guide to Conventional and Alternative Fuel Sources*. M.E. Sharpe Inc., Armonk, New York.
- Pandey, M.P.; Kim, C.S. 2011. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chem. Eng. Technol.*, 34: 29-41.
- Parker, S.P., and Corbitt, R.A. (Editors). 1994. *Encyclopedia of Environmental Science and Engineering*. McGraw-Hill, New York.
- Pfafflin, J.R., and Ziegler, E.N. (Editors). 2006. *Environmental Science and Engineering 5th Edition*. CRC Press, Taylor & Francis Group, Boca Raton, Florida. Volume 1 and Volume 2.
- Shultis, J.K., and Faw, R.E. 2002. *Fundamentals of Nuclear Science and Engineering*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Singh, Y.K. 2006. *Environmental Science*. New Age International Publishers, New Delhi, India.
- Speight, J.G. 2011. *An Introduction to Petroleum Technology, Economics, and Politics*. Scrivener Publishing, Beverly, Massachusetts.
- Speight, J.G. (Editor) 2011. *The Biofuels Handbook*. Royal Society of Chemistry, London, United Kingdom.
- Speight, J.G. 2014. *The Chemistry and Technology of Petroleum 5th Edition*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Speight, J.G., and Islam, M.R. 2016. *Peak Energy – Myth or Reality*. Scrivener Publishing, Beverly, Massachusetts.
- Speight, J.G. 2017. *Handbook of Petroleum Refining*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Speight, J.G. 2019. *Natural Gas: A Basic Handbook 2nd Edition*. Gulf Publishing Company, Elsevier, Cambridge, Massachusetts.
- Speight, J.G. 2019. *Handbook of Petrochemical Processes*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Speight, J.G. 2019. *Biogas: Production and Properties*. Nova Science Publishers, New York.
- Speight, J.G. 2020. *Synthetic Fuels Handbook: Properties, Processes, and Performance 2nd Edition*. McGraw-Hill, New York.
- Speight, J.G. 2020. *Global Climate Change Demystified*. Scrivener Publishing, Beverly, Massachusetts.
- Speight, J.G. 2020. *The Refinery of the Future 2nd Edition*. Gulf Professional Publishing, Elsevier, Oxford, United Kingdom.
- Srivastava, S.P., Hancsók, J. 2014. *Fuels and Fuel Additives*. John Wiley & Sons Inc., Hoboken, New Jersey.
- Taylor, P.W. 1986. *Respect for Nature: A Theory of Environmental Ethics*. Princeton University Press, Princeton University, Princeton, New Jersey.
- Twidell, J., and Weir, A. 2006. *Renewable Energy Resources*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Vernon, R.H. 2004 *A practical Guide to Rock Microstructure*, Cambridge University Press, Cambridge University, Cambridge, United Kingdom.
- Voroney, R.P., and Heck, R.J. 2007. *The Soil Habitat*. In: *Soil microbiology, ecology and biochemistry 3rd Edition* E.A. Paul (Editor). Elsevier, Amsterdam, Netherlands.
- Weiner, R.E., and Matthews, R.A. *Environmental Engineering fourth Edition*. Butterworth Heinemann, Elsevier Science, Burlington, Massachusetts.
- Wenk, H-R., and Bulakh, A. 2004. *Minerals: Their Constitution and Origin*. Cambridge University Press, Cambridge University, Cambridge, United Kingdom.

About the Author

Dr. James G. Speight has doctorate degrees in Chemistry, Geological Sciences, and Petroleum Engineering and is the author of more than 90 books in petroleum science, petroleum engineering, biosciences, and environmental sciences as well as books relating to ethics and ethical issues.

Dr. Speight has more than fifty years of experience in areas associated with (i) the properties, recovery, and refining of reservoir fluids, (ii) conventional petroleum, heavy oil, and tar sand bitumen, (iii) the properties and refining of natural gas, gaseous fuels, crude oil quality, (iv) the production and properties of petrochemicals from various sources, (v) the properties and refining of biomass, biofuels, biogas, and the generation of bioenergy, (vi) reactor and catalyst technology, and (vii) the environmental and toxicological effects arising from the use of energy sources. His work has also focused on safety issues, environmental effects, remediation, reactors associated with the production and use of fuels and biofuels, process economics, as well as ethics in science and engineering and in ethics in the universities.

Although he has always worked in private industry which focused on contract-based work, Dr. Speight has served as a Visiting Professor in the College of Science, University of Mosul (Iraq), Visiting Professor in Chemical Engineering at the Technical University of Denmark, and the University of Trinidad and Tobago as well as adjunct appointments at various universities. He has also served as a thesis examiner for more than 25 theses.

As a result of his work, Dr. Speight has been honored as the recipient of the following awards:

- Diploma of Honor, United States National Petroleum Engineering Society. *For Outstanding Contributions to the Petroleum Industry*, 1995.
- Gold Medal of the Russian Academy of Sciences. *For Outstanding Work in the Area of Petroleum Science*. 1996.
- Einstein Medal of the Russian Academy of Sciences. *In recognition of Outstanding Contributions and Service in the field of Geologic Sciences*. 2001.
- Gold Medal - Scientists without Frontiers, Russian Academy of Sciences. *In recognition of His Continuous Encouragement of Scientists to Work Together across International Borders*. 2005.
- Gold Medal – Giants of Science and Engineering, Russian Academy of Sciences. *In recognition of Continued Excellence in Science and Engineering*. 2006.
- Methanex Distinguished Professor, University of Trinidad and Tobago. *In Recognition of Excellence in Research*. 2007. In 2018, he received the American Excellence Award for Excellence in Client Solutions from the United States Institute of Trade and Commerce, Washington, DC.

Also of Interest

Check out these other related titles from Scrivener Publishing

Green Energy: Solar Energy, Photovoltaics, and Smart Cities, edited by Suman Lata Tripathi and Sanjeevikumar Padmanaban, ISBN 9781119760764. Covering the concepts and fundamentals of green energy, this volume, written and edited by a global team of experts, also goes into the practical applications that can be utilized across multiple industries, for both the engineer and the student. **NOW AVAILABLE!**

Microgrid Technologies, edited by C. Sharmeela, P. Sivaraman, P. Sanjeevikumar, and Jens Bo Holm-Nielsen, ISBN 9781119710790. Covering the concepts and fundamentals of microgrid technologies, this volume, written and edited by a global team of experts, also goes into the practical applications that can be utilized across multiple industries, for both the engineer and the student. **NOW AVAILABLE!**

Energy Storage, edited by Umakanta Sahoo, ISBN 9781119555513. Written and edited by a team of well-known and respected experts in the field, this new volume on energy storage presents the state-of-the-art developments and challenges in the field of renewable energy systems for sustainability and scalability for engineers, researchers, academicians, industry professionals, consultants, and designers. **NOW AVAILABLE!**

Biofuel Cells, Edited by Inamuddin, Mohd Imran Ahamed, Rajender Boddula, and Mashallah Rezakazemi, ISBN 9781119724698. This book covers the most recent developments and offers a detailed overview of fundamentals, principles, mechanisms, properties, optimizing parameters, analytical characterization tools, various types of bio-fuel cells, edited by one of the most well-respected and prolific engineers in the world and his team. **COMING IN SUMMER 2021**

Biodiesel Technology and Applications, Edited by Inamuddin, Mohd Imran Ahamed, Rajender Boddula, and Mashallah Rezakazemi, ISBN 9781119724643. This outstanding new volume provides a comprehensive overview on biodiesel technologies, covering a broad range of topics and practical applications, edited by one of the most well-respected and prolific engineers in the world and his team. **COMING IN SUMMER 2021**

Energy Storage 2nd Edition, by Ralph Zito and Haleh Ardibili, ISBN 9781119083597. A revision of the groundbreaking study of methods for storing energy on a massive scale to be used in wind, solar, and other renewable energy systems. **NOW AVAILABLE!**

Hybrid Renewable Energy Systems, edited by Umakanta Sahoo, ISBN 9781119555575. Edited and written by some of the world's top experts in renewable energy, this is the most comprehensive and in-depth volume on hybrid renewable energy systems available, a must-have for any engineer, scientist, or student. **NOW AVAILABLE!**

Progress in Solar Energy Technology and Applications, edited by Umakanta Sahoo, ISBN 9781119555605. This first volume in the new groundbreaking series, *Advances in Renewable Energy*, covers the latest concepts, trends, techniques, processes, and materials in solar energy, focusing on the state-of-the-art for the field and written by a group of world-renowned experts. **NOW AVAILABLE!**

A Polygeneration Process Concept for Hybrid Solar and Biomass Power Plants: Simulation, Modeling, and Optimization, by Umakanta Sahoo, ISBN 9781119536093. This is the most comprehensive and in-depth study of the theory and

practical applications of a new and groundbreaking method for the energy industry to “go green” with renewable and alternative energy sources. *NOW AVAILABLE!*

Nuclear Power: Policies, Practices, and the Future, by Darryl Siemer, ISBN 9781119657781. Written from an engineer’s perspective, this is a treatise on the state of nuclear power today, its benefits, and its future, focusing on both policy and technological issues. *NOW AVAILABLE!*

Zero-Waste Engineering 2nd Edition: A New Era of Sustainable Technology Development, by M. M. Kahn and M. R. Islam, ISBN 9781119184898. This book outlines how to develop zero-waste engineering following natural pathways that are truly sustainable using methods that have been developed for sustainability, such as solar air conditioning, natural desalination, green building, chemical-free biofuel, fuel cells, scientifically renewable energy, and new mathematical and economic models. *NOW AVAILABLE!*

Sustainable Energy Pricing, by Gary Zatzman, ISBN 9780470901632. In this controversial new volume, the author explores a new science of energy pricing and how it can be done in a way that is sustainable for the world’s economy and environment. *NOW AVAILABLE!*

Sustainable Resource Development, by Gary Zatzman, ISBN 9781118290392. Taking a new, fresh look at how the energy industry and we, as a planet, are developing our energy resources, this book looks at what is right and wrong about energy resource development. This book aids engineers and scientists in achieving a true sustainability in this field, both from an economic and environmental perspective. *NOW AVAILABLE!*

The Greening of Petroleum Operations, by M. R. Islam *et al.*, ISBN 9780470625903. The state of the art in petroleum operations, from a “green” perspective. *NOW AVAILABLE!*

Emergency Response Management for Offshore Oil Spills, by Nicholas P. Cheremisinoff, PhD, and Anton Davletshin, ISBN 9780470927120. The first book to examine the Deepwater Horizon disaster and offer processes for safety and environmental protection. *NOW AVAILABLE!*

Biogas Production, Edited by Ackmez Mudhoo, ISBN 9781118062852. This volume covers the most cutting-edge pretreatment processes being used and studied today for the production of biogas during anaerobic digestion processes using different feedstocks, in the most efficient and economical methods possible. *NOW AVAILABLE!*

Bioremediation and Sustainability: Research and Applications, Edited by Romeela Mohee and Ackmez Mudhoo, ISBN 9781118062845. Bioremediation and Sustainability is an up-to-date and comprehensive treatment of research and applications for some of the most important low-cost, “green,” emerging technologies in chemical and environmental engineering. *NOW AVAILABLE!*

Green Chemistry and Environmental Remediation, Edited by Rashmi Sanghi and Vandana Singh, ISBN 9780470943083. Presents high quality research papers as well as in depth review articles on the new emerging green face of multidimensional environmental chemistry. *NOW AVAILABLE!*

Bioremediation of Petroleum and Petroleum Products, by James Speight and Karuna Arjoon, ISBN 9780470938492. With petroleum-related spills, explosions, and health issues in the headlines almost every day, the issue of remediation of petroleum and petroleum products is taking on increasing importance, for the survival of our environment, our planet, and our future. This book is the first of its kind to explore this difficult issue from an engineering and scientific point of view and offer solutions and reasonable courses of action. *NOW AVAILABLE!*